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VOLUME 1

APRIL 1952

NUMBER 2

PRICE per part 15s. 0d.

PRICE per annum £2 15s. 0d. post free

PRINTED AND PUBLISHED BY TAYLOR & FRANCIS LTD.

RED LION COURT, FLEET ST., LONDON E.C.4

QC1
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Apr
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MONOGRAPHS ON THE PHYSICS AND CHEMISTRY OF MATERIALS

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ADVANCES IN PHYSICS

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Theories of Helium II

By R. B. DINGLE

Royal Society Mond Laboratory, Cambridge

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§ 1. SURVEY OF SALIENT EXPERIMENTAL FEATURES

THE purpose of this article is to review the theories which have been proposed to explain the peculiar properties of liquid helium.* First, however, a short account will be given of some outstanding experimental results.

1.1. PHASE DIAGRAM AND SPECIFIC HEAT CURVE

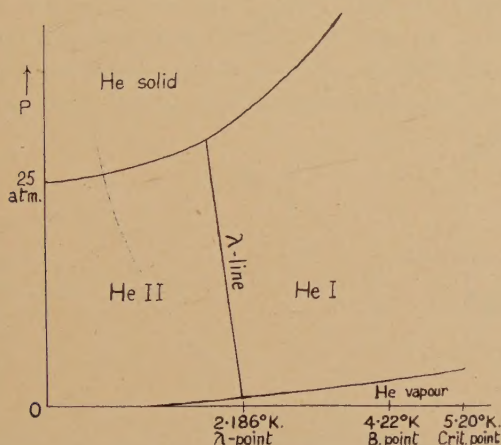
For helium at low temperatures, the diagram in which the equilibrium pressure is plotted against the temperature has the shape shown schematically in fig. 1 (for details see Keesom 1942). Two features of

* The common isotope ${}^4\text{He}$ is meant unless otherwise stated. The rare isotope ${}^3\text{He}$ in the pure liquid state shows hardly any of the anomalous properties exhibited by liquid ${}^4\text{He}$ (see review by Daunt in this issue).

this curve may be emphasized; first, that however much the temperature is lowered, solid helium cannot be formed unless a pressure greater than about 25 atmospheres is applied; and second, that the properties of the liquid state depend on whether the temperature is above or below 2.186°K .

In fact, liquid helium undergoes a phase transition at 2.186°K . Above this temperature the liquid, called He I, behaves much like other liquids, but below 2.186°K liquid helium, called He II, has properties unlike those of any other known liquid. No latent heat is involved in the transition He I \rightleftharpoons He II, as it is for transformations of liquids into vapours and solids into liquids. There is no discontinuity in the entropy, as in ordinary transformations, but there is in the specific heat. The peculiar plot

Fig. 1



Phase diagram.

shown in fig. 2 of the specific heat against temperature for liquid helium* (and similar curves exhibited by certain other substances), has led to this type of transition† being termed a 'lambda-point'.

* Keesom and Keesom (1936), Keesom and Westmijze (1941), Hull, Wilkinson and Wilks (1951), Kramers (1951). See also Keesom (1942), Gorter, Kasteleijn and Mellink (1950).

The fact that the specific heat *decreases* with rise in temperature in the region immediately above the lambda-point has been ascribed to fluctuations—i.e. inclusions of He II (with its anomalously high specific heat) persisting above the lambda-point (Keesom 1942, Pippard 1951). Pippard suggests that scattering by the inclusions of He II, which has a negative coefficient of expansion in contrast to the positive value for He I, may be responsible for the strong attenuation of ordinary sound observed near the lambda-point (Pellam and Squire 1947, Atkins and Chase 1951).

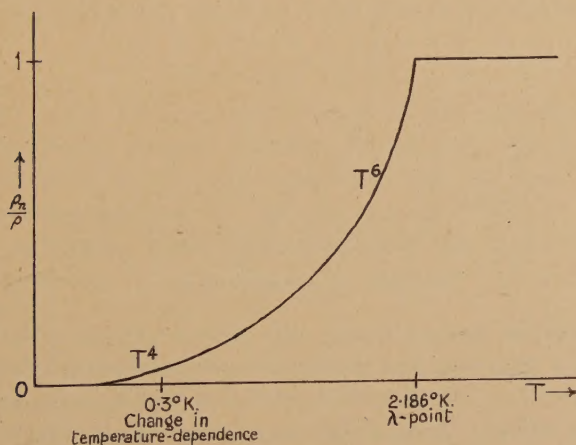
† For discussions of types of transition, see Ehrenfest (1933), Landau and Lifshitz (1938), Keesom (1942), Tisza (1949), Smoluchowski, Mayer and Weyl (1952).

be mentioned that this result holds only when the velocity of the superfluid is small. The maximum velocity for which superfluidity is exhibited is called the 'critical velocity', and is usually of the order of a few centimetres per second (see, for instance, Atkins 1951, and his review in this issue).

1.3. ANDRONIKASHVILI'S EXPERIMENT

There is another method for estimating the ratio of the two 'parts', normal and superfluid. In the experiments of Andronikashvili (1946, 1948 a) and Hollis-Hallett (1950, 1952), a set of parallel horizontal vanes suspended in He II by means of a fine torsion thread were allowed to oscillate in the liquid, and the period of the oscillations determined. The gaps between the vanes and the frequency of oscillation are both so small that the 'part' of the liquid which has viscosity (normal fluid) all clings to the vanes, while the 'part' without viscosity (superfluid) does not, so that the apparent moment of inertia, to which the square of the period is proportional, may be used to calculate the relative amounts of the two 'parts' as a function of temperature (shown schematically in fig. 3).

Fig. 3



Andronikashvili experiment. ρ_n/ρ = fractional effective mass of 'part' clinging to vanes. The temperature-dependences below 1.5°K are theoretical estimates.

1.4. FOUNTAIN EFFECT

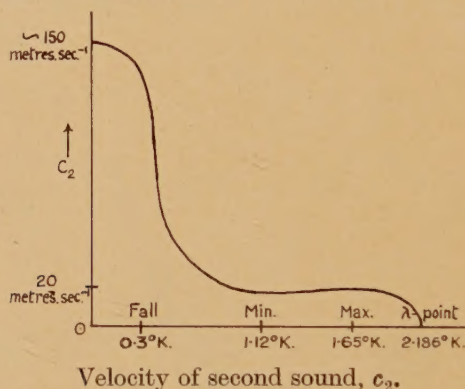
In the fountain effect (Allen and Jones 1938 ; Allen and Reekie 1939 ; Kapitza 1941 ; Duyckaerts 1943 ; Meyer and Mellink 1947 ; Keesom and Duyckaerts 1947 ; Mellink 1947), a difference in temperature is created between two vessels which are connected by a capillary or slit so fine that only superfluid can move along within it. Then a pressure difference will be set up if the entropies of the two 'parts' are different, because the superfluid will tend to move in such a direction as to nullify the imposed

temperature difference. It is found that the superfluid moves towards the high temperature side, showing that it has the lower entropy—an entropy so small, in fact, as to be unmeasurable (Kapitza 1941). The theory of the fountain effect was first given by H. London (1938, 1939). The inverse effect, called the mechano-caloric effect, has been observed by Daunt and Mendelssohn (1939 a).

1.5. SECOND SOUND

The tendency for any temperature difference to be equalized out by convection of the normal and superfluids shows that some potential energy must be associated with *relative* displacement of normal and superfluid. A novel type of wave-motion is therefore possible in He II, one in which this potential energy is periodically transformed into kinetic energy and then back again. Such a wave-motion is called 'second sound', or a 'temperature wave', and may be propagated almost independently of ordinary 'first sound', or a 'pressure-wave'.

Fig. 4



The existence of second sound was demonstrated experimentally by Peshkov (1946) following the theoretical predictions of Tisza (1938, 1940) and Landau (1941). The observed dependence of velocity on temperature is shown schematically in fig. 4 (Peshkov 1946, 1948 b; Fairbank, Fairbank and Lane 1947; Pellam 1949 a; Pellam and Scott 1949; Maurer and Herlin 1949, 1951; Atkins and Osborne 1950).

1.6. HEAT TRANSPORT

The heat conductivity of He I is quite normal, and it is possible to define a coefficient of thermal conductivity which does not vary appreciably with the temperature gradient (Keesom and Keesom 1936). On the other hand, in He II the heat flow is proportional not to $\text{grad } T$ but approximately to $(\text{grad } T)^{1/3}$, so that the coefficient of thermal conductivity would formally be proportional to $(\text{grad } T)^{-2/3}$, becoming very large for small temperature gradients (Allen, Peierls and Uddin 1937; Keesom, Keesom and Saris 1938; Keesom and Saris 1940; Keesom, Saris and Meyer 1940; Duyckaerts 1943; Keesom and Duyckaerts 1947; Mellink

1947). The explanation, first given by Tisza (1938, 1940), is that the heat flow in He II is due to a convection process rather than to ordinary thermal conduction. The superfluid flows towards the high temperature side, and the normal fluid towards the low temperature side, the efficiency of heat transport being limited solely by irreversible processes.

1.7. HELIUM FILMS

He II forms a thick surface film, about a hundred atoms thick, which can flow without friction over surfaces in contact with the bulk liquid (Rollin 1936 ; Kikoin and Lasarew 1939 ; Daunt and Mendelssohn 1938, 1939 b ; Strelkow 1940 ; for recent work, see review article by Jackson in this issue). As in the case of capillary flow, the 'part' of the liquid which is actually flowing is identified with the superfluid, and there is a saturation velocity above which superfluidity is no longer exhibited.

§ 2. ZERO-POINT ENERGY AND THE LIQUID STATE

2.1. LIQUID-SOLID TRANSFORMATION

Solid helium cannot be formed from the liquid merely by a lowering of the temperature ; a pressure of about 25 atmospheres is necessary in addition. Put another way, it is essential to decrease the volume of the assembly before the solid becomes the more stable state. The situation may be summed up (Simon 1934) by the application of the thermodynamic relation

$$T \Delta S = \Delta U + P \Delta V \quad (1)$$

where ΔS , ΔU and ΔV refer respectively to the differences in entropy, internal energy and volume between liquid and solid. By Nernst's theorem, $\Delta S \rightarrow 0$ as $T \rightarrow 0$, and experiment shows that ΔV remains positive, the solid having the smaller volume. Hence ΔU must be negative at sufficiently low temperatures—i.e. the liquid must have the lower internal energy. Actually, ΔU is negative below 1.72° K (Simon and Swenson 1950, Swenson 1950).

In ordinary non-polar solids and liquids, there are two important forces, the long-range van der Waals attraction and the short-range repulsion. The balance of these, determined by the condition of minimum free energy, determines the equilibrium configuration. However, for solids and liquids composed of atoms of small atomic mass (e.g. hydrogen and helium), a third force becomes important, an effective repulsion arising from the zero-point energy due to the atoms being confined in space. The effect of this energy is to keep the atoms as far apart as possible, thereby hindering the attractive forces from becoming strong enough to produce solidification. The magnitude of this zero-point energy may be estimated from Trouton's rule, from the Debye theory, and from a consideration of the balance of forces.

2.2. TROUTON'S RULE

In its usual form, this rule states that the quotient of the latent heat of vaporization per gram molecule and the absolute temperature of ebullition is about 21. This means that the change in entropy on

vaporization is about the same for all substances, a result ultimately depending on the facts that the molecular volume of all gases is the same, and that the entropy of a liquid is negligible compared with that of its vapour. For atoms of low atomic weight, it is necessary to add the zero-point energy to the latent heat, since this energy no longer exists in the vapour state, the atoms being then no longer confined (Bennewitz and Simon 1923). The boiling-point of liquid helium is about 4°K , and the latent heat about 20 calories per gram molecule, so that the zero-point energy U_0 is given by equating $(20+U_0)/4$ to 21, whence

$$U_0 \sim 60 \text{ cal/g mol.} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

2.3. ZERO-POINT ENERGY ON THE DEBYE MODEL

The mean energy of a linear harmonic oscillator of frequency ν is

$$\frac{1}{2}h\nu + \frac{h\nu}{\exp(h\nu/kT) - 1}, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

the first term giving the zero-point energy per oscillator. On the Debye model, the total zero-point energy per gram molecule is therefore

$$U_0 = 3N \int_0^{k\Theta/h} \frac{1}{2}h\nu \frac{4\pi\nu^2 d\nu}{c^3} \bigg/ \int_0^{k\Theta/h} \frac{4\pi\nu^2 d\nu}{c^3} = \frac{9R\Theta}{8}, \quad . \quad . \quad . \quad (4)$$

where Θ is the Debye characteristic temperature. For He I specific heat measurements show that $\Theta \sim 30^{\circ}\text{K}$, so that $U_0 \sim 60 \text{ cal/g mol}$, a value which agrees with that deduced from Trouton's rule.

2.4. ZERO-POINT ENERGY AND THE BALANCE OF FORCES

The zero-point energy may be estimated theoretically in two limiting cases. When the interatomic distance l is less than the atomic diameter a , each atom of mass m may be considered as trapped within a sphere of radius $l-a$ formed by the neighbouring atoms. The Schrödinger equation for the problem then gives

$$U_0 = Nh^2/8m(l-a)^2, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where N is Avogadro's number. On the other hand, when the interatomic distance is much greater than the atomic diameter, each atom may be imagined to be surrounded by a sphere, radius b , of volume equal to the atomic volume divided by N . The quantity b depends on the structure, in particular on the coordination number: for a simple cubic lattice $4\pi b^3/3 = l^3$. The wave-function must vanish at $r=a$, since two atoms cannot approach to within a distance smaller than the atomic diameter, and the gradient of the wave-function must vanish when $r=b$, since each 'atomic sphere' is merely a copy of its neighbour. The zero-point energy per gram molecule is then found to be approximately (Heitler 1927; see also Lenz 1929 and Dingle 1949):

$$U_0 = \frac{3Nh^2}{8\pi^2m} \frac{a}{(b-a)^3} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

For He II, $a \approx 3 \times 10^{-8}$ cm, $l \approx 3.6 \times 10^{-8}$ cm, so that neither of these extreme cases is quantitatively applicable, though the order of magnitude is given correctly. F. London (1936) has used an interpolation formula between these limiting relations (5) and (6).

The zero-point energy depends on the value of b , the radius of the atomic sphere, and is therefore a function of the structure. For equilibrium, the sum of three forces must be equated to zero. Two of these are derived from the expression for the potential energy V between two helium atoms (Slater and Kirkwood 1931):

$$V = \{7.7 \exp(-2.43r/a_0) - 0.68(r/a_0)^{-6}\} \times 10^{-10} \text{ ergs}, \quad (7)$$

where a_0 is the Bohr radius of hydrogen, equal to 0.529×10^{-8} cm. The third 'force' is that arising from the zero-point energy. F. London (1936) calculated and minimized the total energy for several possible structures, and concluded that if He II tended to form any of these, the diamond lattice would be the one most favoured. However, he pointed out that, owing to the continual movement of the particles under their zero-point energy, any structure assigned to He II could only be regarded as a statistical one—i.e. one in which the 'lattice points' would only give an indication of the positions for which the probability of finding an atom would be higher than elsewhere.

Pekris (1950) has given a similar calculation, based on the theory of liquids of Lennard-Jones and Devonshire (1937). He concludes that the best agreement with experiment is obtained if the coordination number is about 9.5.

§3. ORIGIN OF THE LAMBDA-POINT

3.1. THEORIES BASED ON ORDER-DISORDER TRANSITIONS

3.11. Fröhlich's Theory

Fröhlich (1937) made the ingenious suggestion that since two diamond lattices shifted by one spacing are equivalent to one body-centred cubic lattice, an order-disorder transition would be possible in which each point of the body-centred lattice is 'half-occupied' at a temperature above the transition point, but below, the atoms are in *one* of the diamond lattices. Fröhlich suggested that perhaps He II had the diamond structure as supposed by London, and He I the body-centred. The total entropy change in such a transition would be about $R \ln 2$ cal/deg/g mol, which is of the observed order of magnitude for the entropy of liquid helium at its boiling point, by which temperature the transition may be considered as practically complete.

3.12. Jones' Theory

H. Jones (1938), in an attempt to explain the negative coefficient of thermal expansion of He II, made an explicit calculation of the entropy-temperature curve on the assumption that the total entropy is of the form

$$S = S_{\text{Debye}}(T/\Theta) + S_{\text{Disorder}}(T/\Delta), \quad (8)$$

where Δ is the ordering energy, which on the Bragg-Williams theory is a function of volume alone.

If the second term in (8) is dominant, the coefficient of thermal expansion is easily shown to be

$$\alpha = -C_v \chi \beta / V, \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where $\beta = d(\ln \Delta)/d(\ln V)$, C_v is the specific heat at constant volume, χ the isothermal compressibility and V the volume. An independent estimate of β is obtained from the consideration that along the lambda-line (the line separating He I from He II in the phase diagram) the entropy is approximately constant (see Keesom 1942). Hence if $S = S(T/\Delta)$, $\Delta \propto T_\lambda$ along the lambda-line, so that

$$\beta = d(\ln \Delta)/d(\ln V) = d(\ln T_\lambda)/d(\ln V_\lambda), \quad . \quad . \quad . \quad (10)$$

where V_λ is the volume at the lambda-point, there being no discontinuity in the volume. Rough agreement with experiment is obtained, especially if a small Debye entropy is assumed in addition to the entropy of disorder.

Jones interpreted the anomalous heat flow in He II as a convection process related to the flow of disorder, 'wrong atoms' flowing from higher to lower temperatures.

3.13. Comments on Order-Disorder Theories

F. London (1938 a, 1939) criticized these order-disorder theories on the grounds that it is difficult to see why atoms should prefer to settle in *one* of the two available lattices assumed to exist in He II. For instance, suppose a transition were taking place from the body-centred lattice representing He I to one of the diamond lattices representing He II. Then it is necessary to show that if some atoms do go into the lattice points of one of the diamond lattices, the remainder will prefer to go into the *same* lattice. London showed that this was not true for the diamond lattice if the effects of second nearest neighbours were taken into account.

It is, in any case, doubtful whether any sufficiently real structure to account for order-disorder effects could form in a liquid in which the zero-point energy is of such importance as in He II. The x-ray patterns (Keesom and Taconis 1938, Reekie 1940, 1947) for both He I and He II are of the usual diffuse type characteristic of liquids, and there appears to be no real evidence of a structural change at the lambda-point. It must be borne in mind, however, that many structures give similar x-ray patterns, so that the available experimental data do not rule out the possibility of a change in structure. Also, it must be remembered that in a transition which involves no latent heat (transition of 'second order') the structural change would be gradual. According to Keesom and Taconis (1938), the pattern found for He II is actually inconsistent with a structure of precisely the diamond type, but other similar structures may be pictured which are consistent with it. On the other hand, Reekie (1947) has stated that the diamond (and simple cubic) structures give the best fit with his experimental data.

Finally, it must be remarked that it would also be necessary to explain why a similar order-disorder transition should not occur in liquid ${}^3\text{He}$, which, in fact, does not display such anomalous properties as liquid ${}^4\text{He}$.

3.2. THEORY OF BOSE-EINSTEIN CONDENSATION

3.21. Bose-Einstein Condensation of an Ideal Gas

F. London (1938 a, b; 1939) suggested that the lambda-point in the specific heat of liquid ${}^4\text{He}$ might be related to a curious property of an assembly obeying Bose-Einstein (but not Fermi-Dirac) statistics, which was first noticed by Einstein (1924, 1925). It has been shown experimentally that the rare isotope ${}^3\text{He}$, which should obey Fermi-Dirac statistics since there are an odd number of particles in its nucleus, neither has a lambda-point nor shows superfluid properties down to a temperature of about 0.25°K (Daunt and Heer 1950); this suggests very strongly that the behaviour of the common isotope ${}^4\text{He}$ is indeed to be correlated with the fact that it obeys Bose-Einstein statistics.

The usual demonstrations of Bose-Einstein condensation are based on the well-known formula

$$\bar{n}_i = \frac{1}{\xi \exp(E_i/kT) - 1} \quad \dots \quad (11)$$

for the mean occupation numbers \bar{n}_i of a non-degenerate energy level E_i (London 1938 a, b; 1939); an alternative treatment uses the equivalent partition function (Fowler and Jones 1938). ξ is a parameter, independent of the state label i , determined by the condition $N = \sum \bar{n}_i$; this expresses the fact that the total number of particles in the assembly is equal to the sum of the numbers of particles on each of the energy levels. For an ideal Bose-Einstein gas composed of particles of mass m , $E(p) = p^2/2m$, and the number of states per unit momentum range is asymptotically equal* to $4\pi p^2 V dp / h^3$ for a volume V . Thus at first sight it would appear that

$$N = \frac{4\pi V}{h^3} \int_0^\infty \frac{p^2 dp}{\xi \exp(p^2/2mkT) - 1} = \frac{4\pi V}{h^3} (2mkT)^{3/2} \int_0^\infty \frac{x^2 dx}{\xi \exp(x^2) - 1} \quad (12)$$

In order to admit only positive occupation numbers in \bar{n}_i , it is essential that† $\xi \geq 1$, so that the right-hand side of (12) has a *maximum value* equal to

$$\frac{4\pi V}{h^3} (2mkT)^{3/2} \int_0^\infty \frac{x^2 dx}{\exp(x^2) - 1} = \frac{2.612V(2\pi mkT)^{3/2}}{h^3} \quad (13)^\ddagger$$

* Meaning that the de Broglie wavelength corresponding to the momentum is much less than the linear dimensions of the assembly, i.e. $p = h/\lambda \gg hV^{-1/3}$.

† Here we have (for convenience) taken the lowest state as of zero energy. All energies are then to be measured as excesses over the zero-point energy.

‡ $\int_0^\infty x^2 dx \exp(-x^2) / [1 - \exp(-x^2)] = \int_0^\infty x^2 dx \exp(-x^2) [1 + \exp(-x^2) + \dots]$
 $= \int_0^\infty x^2 dx \exp(-x^2) (1 + 2^{-3/2} + \dots) = \frac{1}{4} \sqrt{\pi} \zeta(3/2),$

where ζ is the Riemann zeta-function; $\zeta(3/2) = 2.612$.

We have then to ask what happens if the number of particles exceeds this number. As might be expected, the difficulty has arisen only because of the approximations made, for it is clear from (11) that any number of particles could be accommodated in the assembly. There is, for instance, no limit to the number, $\bar{n}_0 = 1/(\xi - 1)$, which can be accommodated in the lowest state $E=0$, for it is only necessary to take ξ sufficiently close to unity. The fallacy in the derivation of (12) is simply that the statistical weight of the lowest state $E=0$ has been taken as zero (since $p=0$) instead of unity as it should be. If the lowest state is to be included with its proper statistical weight, (12) must be replaced by

$$N = \frac{1}{\xi - 1} + \frac{4\pi V}{h^3} (2mkT)^{3/2} \int_0^\infty \frac{x^2 dx}{\xi \exp(x^2) - 1} = N_s + N_n, \quad (14)$$

in which we have provisionally identified the particles in the ground state with the 'superfluid', and those in excited states with the 'normal fluid'. Thus a change in the properties of the assembly occurs at the temperature T_λ for which the first term in (14) becomes important, i.e. when

$$\frac{N}{V} = \frac{2.612(2\pi mkT_\lambda)^{3/2}}{h^3}. \quad (15)$$

It is interesting to note that for liquid helium this relation, really valid only for an ideal gas, gives $T_\lambda = 3.14^\circ \text{K}$, quite close to the experimental value for liquid ${}^4\text{He}$, $T_\lambda = 2.186^\circ \text{K}$. Such rough agreement should not be taken too seriously, however, because the theory of dimensions ensures that practically *all* characteristic temperatures should be of the order of $k^{-1}\rho^{2/3}\hbar^2m^{-5/3}$, where ρ is the density.

For $T < T_\lambda$, $\xi \simeq 1$, and we may take

$$N_n = \frac{4\pi V}{h^3} \int_0^\infty \frac{p^2 dp}{\exp(p^2/2mkT) - 1} = N \left(\frac{T}{T_\lambda} \right)^{3/2}, \quad (16)$$

$$N_s = \frac{1}{\xi - 1} = N \left\{ 1 - \left(\frac{T}{T_\lambda} \right)^{3/2} \right\}. \quad (17)$$

Thus as the temperature is lowered, more and more particles 'condense' into the lowest state. Only the remainder, the particles in excited states, contribute towards the internal energy of the assembly, given by

$$U = \frac{4\pi V}{h^3} \int_0^\infty \frac{(p^2/2m)p^2 dp}{\exp(p^2/2mkT) - 1} = 0.770 NkT \left(\frac{T}{T_\lambda} \right)^{3/2}. \quad (18)$$

The specific heat at constant volume, $C_v = (\partial U / \partial T)_v$, and the entropy $S = \int_0^T C_v dT/T$ are thus

$$C_v = 1.926 Nk(T/T_\lambda)^{3/2}; \quad S = 1.284 Nk(T/T_\lambda)^{3/2}. \quad (19)$$

It is interesting to note that (19) would give for the entropy at the lambda-point $S_\lambda = 1.284 Nk$, as compared to the experimental value $S_\lambda \simeq 0.8 Nk$ for liquid $\frac{4}{2}\text{He}$.

For $T > T_\lambda$, N_s is negligible, and we may take

$$N = \frac{4\pi V}{h^3} \int_0^\infty \frac{p^2 dp}{\xi \exp(p^2/2mkT) - 1}; \quad U = \frac{4\pi V}{h^3} \int_0^\infty \frac{(p^2/2m)p^4 dp}{\xi \exp(p^2/2mkT) - 1}. \quad (20)$$

Such integrals cannot be evaluated explicitly, but the following series are obtained:

$$U = \frac{3}{2} NkT \{1 - 0.462(T_\lambda/T)^{3/2} - 0.0226(T_\lambda/T)^3 \dots\}, \quad (21)$$

$$S = \frac{3}{2} Nk \{1.0265 - \ln(T_\lambda/T) - 0.154(T_\lambda/T)^{3/2} \dots\}, \quad (22)^*$$

$$C_v = \frac{3}{2} Nk \{1 + 0.231(T_\lambda/T)^3 + 0.045(T_\lambda/T)^3 \dots\}. \quad (23)$$

The theory for an ideal gas thus leads to some sort of lambda-point at approximately the observed temperature for liquid helium, and to an entropy at the lambda-point of about the observed magnitude. It is hardly surprising to find, however, that there are pronounced discrepancies between the theoretical predictions for this ideal Bose-Einstein gas and those found experimentally for $\frac{4}{2}\text{He}$. For instance, the ideal gas theory leads to a *third-order* transition, a transition in which neither the entropy nor the specific heat shows a discontinuity, whilst the transition in liquid helium seems to be of *second-order*, a transition with a discontinuity in the specific heat. Again, for $T < T_\lambda$, the ideal gas theory leads to the expression $C \propto T^{1.5}$, as opposed to the observed relation $C \propto T^6$ for $T \gtrsim 0.6^\circ \text{K}$.

3.211. Transport Phenomena and Thermal Waves in a Bose-Einstein Gas.—Band has discussed the theory of transport phenomena (1949 a), the propagation of thermal waves (1949 c) and heat transfer (1950), in a Bose-Einstein gas.

3.212. Gentile's 'Intermediate Statistics'.—Some authors have considered it convenient to regard Bose-Einstein statistics as a limiting case of a general scheme in which the maximum possible occupation number per state lies between unity (Fermi-Dirac) and infinity (Bose-Einstein). For the basic theory, see Gentile (1940, 1941, 1942); Sommerfeld (1942, 1946); Schubert (1946, 1947); and Wergeland (1944). For applications to He II, see also Salvetti (1941) and Caldirola (1943).

3.22. Bose-Einstein Condensation of a Liquid

A considerable improvement in the theory may be achieved by assuming that each particle moves in a self-consistent field formed by its neighbours.

* See Keesom (1942).

As an *ad hoc* generalization of the perfect gas spectrum $E(p)=p^2/2m$, we may take $E(p)=Ap^{1/r}$, where A and r are parameters.* Then below the lambda-point, given by $N=N_n$,

$$N_n = \frac{4\pi V}{h^3} \int_0^\infty \frac{p^2 dp}{\exp(Ap^{1/r}/kT) - 1} = \frac{4\pi V}{h^3} \left(\frac{kT}{A}\right)^{3r} r \int_0^\infty \frac{x^{3r-1} dx}{\exp(x) - 1} \\ = \frac{4\pi r V}{h^3 A^{3r}} \Gamma(3r) \zeta(3r) (kT)^{3r}, \quad (24)$$

$$U = \frac{4\pi r V}{h^3 A^{3r}} \Gamma(3r+1) \zeta(3r+1) (kT)^{3r+1}, \quad (25)$$

$$S = \frac{4\pi k V}{3h^3 A^{3r}} \Gamma(3r+2) \zeta(3r+1) (kT)^{3r}, \quad (26)$$

$$C_v = \frac{4\pi k r V}{h^3 A^{3r}} \Gamma(3r+2) \zeta(3r+1) (kT)^{3r}, \quad (27)$$

where ζ is the Riemann zeta-function, and Γ the gamma-function.

Above the lambda-point,

$$N = \frac{4\pi V}{h^3} \left(\frac{kT}{A}\right)^{3r} r \int_0^\infty \frac{x^{3r-1} dx}{\xi \exp(x) - 1}, \quad (28)$$

$$U = \frac{4\pi V k T}{h^3} \left(\frac{kT}{A}\right)^{3r} r \int_0^\infty \frac{x^{3r} dx}{\xi \exp(x) - 1}, \quad (29)$$

3.221. *Discontinuity in the Specific Heat*.—When $\xi \simeq 1$, i.e. immediately above the lambda-point, and $r > 2/3$,†

$$\int_0^\infty \frac{x^{3r-1} dx}{\xi \exp(x) - 1} \simeq \int_0^\infty \frac{x^{3r-1} dx}{\exp(x) - 1} - (\xi - 1) \int_0^\infty \frac{\exp(x) x^{3r-1} dx}{[\exp(x) - 1]^2} \\ = \Gamma(3r) \zeta(3r) \left\{ 1 - \frac{(\xi - 1) \zeta(3r - 1)}{\zeta(3r)} \right\}. \quad (30)$$

* F. London (1939) takes the density of states per unit energy range and the number of atoms in 'Bloch states' as parameters. The author prefers the assumption $E(p)=Ap^{1/r}$, since particular models then appear directly as special cases. For instance, the perfect gas model corresponds to $A=1/2m$ and $r=1/2$, and the Debye model to $A=c$ (velocity of sound) and $r=1$.

F. London (1943) has also attempted to calculate the correlation effect on the distribution of molecular distances.

Wergeland (1947) has noted that a Bose-Einstein condensation can take place only if the particles are not localized in the structure, i.e. only if their potential energy is small compared with the thermal and zero-point energies.

† If $r \leq 2/3$ the integrals may be evaluated by methods due to Opechowski (1937) and Robinson (1951), but the results do not seem to have any application to liquid helium in this particular connection.

Since N is constant, $\xi - 1 \asymp \frac{\zeta(3r)}{\zeta(3r-1)} \left[1 - \left(\frac{T_\lambda}{T} \right)^{3r} \right]$ (31)

Similarly

$$U \propto T^{3r+1} \left\{ 1 - (\xi - 1) \frac{\zeta(3r)}{\zeta(3r+1)} \right\}, \quad (32)$$

so that just above the lambda-point the specific heat is

$$\begin{aligned} C_+ = \left(\frac{\partial U}{\partial T} \right)_v &\propto (3r+1) T_\lambda^{3r} - \frac{\zeta(3r)}{\zeta(3r+1)} T_\lambda^{3r+1} \left[\frac{\partial(\xi-1)}{\partial T} \right]_{T=T_\lambda} \\ &= (3r+1) T_\lambda^{3r} \left\{ 1 - \frac{3r}{3r+1} \frac{\{\zeta(3r)\}^2}{\zeta(3r-1)\zeta(3r+1)} \right\}. \quad . . . (33) \end{aligned}$$

Below the lambda-point the second term in (33) is missing, since ξ is then equal to unity and thus independent of temperature. The ratio of the specific heat just above the transition point to that just below is therefore

$$\frac{C_+}{C_-} = 1 - \frac{3r}{3r+1} \frac{\{\zeta(3r)\}^2}{\zeta(3r-1)\zeta(3r+1)}. \quad (34)^*$$

Thus the introduction of interactions between the particles within the assembly leads to a discontinuity in the specific heat at the transition point. Since $S = (U - F)/T$, where the internal energy U and Helmholtz free energy F are analytic functions of T , there cannot be any latent heat associated with the transition. This is also clear physically, since as $T \rightarrow T_\lambda$, $N_s \rightarrow 0$, so that in the limit no further particles are required to change their state, and thus no energy is needed.

Since for liquid helium $C \propto T^6$ for $T \gtrsim 0.6^\circ \text{K}$, we must take $r \sim 2$. On this assumption, the specific heat jumps by about 15% at the lambda-point. This discontinuity is much smaller than that observed, and it must be concluded that this theory cannot be applied quantitatively at temperatures close to the lambda-point.

3.222. *Alternative Form of Self-consistent Field.*—In the treatment given above, the energy-momentum relation has arbitrarily been supposed to be a simple power law. It is plausible to argue, however, that a particle must overcome some potential barrier Δ before it can move sufficiently freely to be considered as ‘quasi-free’. On such an assumption, the energy spectrum is of the form (cf. Bijl 1940; Bijl, de Boer and Michels 1941)

$$E = \Delta + p^2/2\mu, \quad (35)$$

or zero, μ being the effective mass of the quasi-free particles.† Assuming (35), it is easily found that below the lambda-point,

* A similar expression was found by F. London (1939).

† This energy spectrum is identical with that introduced by Landau (1941) for rotons (§3.31). Since $\xi = 1$ both for a condensed Bose-Einstein assembly and for an assembly of non-material excitations such as rotons, the statistical consequences are also the same for the two cases, if rotons obey Bose-Einstein statistics.

$$N_n = \frac{V(2\pi\mu kT)^{3/2}}{h^3} \exp(-\Delta/kT) f_{3/2}(T), \quad \dots \quad (36)$$

$$U = \frac{kTV(2\pi\mu kT)^{3/2}}{h^3} \exp(-\Delta/kT) \left\{ \frac{3}{2} f_{5/2}(T) + \frac{\Delta}{kT} f_{3/2}(T) \right\}, \quad \dots \quad (37)$$

$$S = \frac{kV(2\pi\mu kT)^{3/2}}{h^3} \exp(-\Delta/kT) \left\{ \frac{5}{2} f_{5/2}(T) + \frac{\Delta}{kT} f_{3/2}(T) \right\}, \quad \dots \quad (38)$$

$$C_v = \frac{kV(2\pi\mu kT)^{3/2}}{h^3} \exp(-\Delta/kT) \left\{ \frac{15}{4} f_{5/2}(T) + \frac{3\Delta}{kT} f_{3/2}(T) + \left(\frac{\Delta}{kT} \right)^2 f_{1/2}(T) \right\}. \quad \dots \quad (39)$$

where

$$f_n(T) = 1 + \frac{\exp(-\Delta/kT)}{2^n} + \frac{\exp(-2\Delta/kT)}{3^n} + \dots, \quad \dots \quad (40)$$

provided this series converges.*

On this model, the jump in the specific heat at the lambda-point is

$$\frac{C_+}{C_-} = \frac{\frac{15}{4} f_{5/2}(T_\lambda) - \frac{9}{4} \frac{f_{3/2}^2(T_\lambda)}{f_{1/2}(T_\lambda)} + \frac{3}{2} \left(\frac{\Delta}{kT_\lambda} \right) f_{3/2}(T_\lambda) + \left(\frac{\Delta}{kT_\lambda} \right)^2 f_{1/2}(T_\lambda)}{\frac{15}{4} f_{5/2}(T_\lambda) + 3 \left(\frac{\Delta}{kT_\lambda} \right) f_{3/2}(T_\lambda) + \left(\frac{\Delta}{kT_\lambda} \right)^2 f_{1/2}(T_\lambda)}. \quad \dots \quad (41)$$

Comparison of (39) with the observed specific heat of He II gives $\mu/m_{\text{He}} \sim 7-8$ and $\Delta/k \sim 8-9^\circ\text{K}$ (see §3.31). The quantity $\exp(-\Delta/kT)$ is therefore always small, and we may take all f 's as approximately equal to unity. Eqn. (41) then gives $C_+/C_- \sim \frac{2}{3}$; the theoretical discontinuity in the specific heat is again rather smaller than that observed.

3.23. Comments on the Theory of Bose-Einstein Condensation

The most serious objection to the foregoing theory lies in its basic starting point—the ideal gas approximation. Matters are considerably improved by the introduction of a self-consistent field, but this still fails to take any account of correlations between the positions of the individual particles in the assembly. It is not altogether surprising, therefore, that there are still marked divergences between theory and experiment: for instance, $(\partial T_\lambda / \partial V)_N$ is given as negative, in contradiction to experiment.

Some of these correlations give rise to the ordinary Debye specific heat, and it is thus plausible to suppose that these at least might be taken into account simply by adding the Debye terms on to those calculated in the last sections. Since the temperatures with which we are concerned are much smaller than the Debye temperature, these ‘phonon’ contributions are, per unit mass of liquid,

$$U_{\text{phon}} = \frac{4}{15} \frac{\pi^5 k^4 T^4}{\rho h^3 c^3}; \quad S_{\text{phon}} = \frac{16}{45} \frac{\pi^5 k^4 T^3}{\rho h^3 c^3}; \quad C_{\text{phon}} = \frac{16}{15} \frac{\pi^5 k^4 T^3}{\rho h^3 c^3}, \quad \dots \quad (42)$$

where c is the velocity of ordinary sound in the liquid and ρ the density.

* If it does not converge, the corresponding integrals may be evaluated by the methods of Opechowski (1937) and Robinson (1951).

Here it has been assumed that only longitudinal waves can pass through liquid helium. This is very probably true at extremely low temperatures where the important phonon frequencies $\nu \sim kT/h$ are relatively small, but it may not remain true at higher temperatures (but see below). In this connection, Temperley (1952) has made the suggestion that Landau's rotons (§ 3.31) might be replaced by quantized shear (transverse) waves.

Since the specific heat of He II above about 0.6°K is roughly proportional to T^6 , corresponding to values of the parameters introduced into the self-consistent fields of $r \sim 2$ (§ 3.22) and $\Delta \sim 8-9^\circ \text{K}$ (§ 3.222), the phonon contributions given by (42) should become dominant at temperatures below about 0.6°K , since they are proportional to lower powers of T . This is, in fact, what is observed experimentally, the specific heat below about 0.6°K being proportional to T^3 (Kramers 1951). Moreover, the fact that the proportionality constant is steady over a large temperature range (at least down to 0.25°K) suggests that rather than giving a contribution varying with the temperature, transverse waves give either a complete contribution, or no contribution at all. Only the latter alternative is compatible with the known velocity of ordinary sound (longitudinal waves) in He II at very low temperatures.

It is perhaps worth emphasizing that of all liquids, liquid helium behaves most like a gas. Not only is its density unusually low, but its viscosity is of the gaseous type, rising with temperature instead of falling as does the viscosity of a normal liquid. (This remark refers primarily to He I, for, as pointed out in § 1.2, there are special reasons why the apparent viscosity of He II should decrease with temperature.) It may be added that the isotope ^3He also shows gas-like properties in its liquid state; for instance, its specific heat is roughly proportional to the absolute temperature, just like a Fermi-Dirac gas. These gas-like properties of liquid helium arise because the high zero-point energy (§ 2) forces the particles far apart. It is probable, therefore, that the gas approximation is not quite so inadequate as might appear at first sight.

Another objection is that the arguments of § 3.21 do not make it at all clear why the 'excess particles' should be accommodated in the single state of lowest energy, rather than be distributed amongst all the lower states. Assuming that $\bar{n}_i = 1/[\xi \exp(E_i/kT) - 1]$, or rather the equivalent partition function, Fowler and Jones (1938) avoided the rather artificial splitting of the summation determining ξ into one term corresponding to the ground state and an integral corresponding to the excited states. Making use of inequalities obtained by transformations of theta-functions, they constructed a rigorous argument, leading to precisely the same conclusions as those given in § 3.21 based on the simpler method of F. London (1938 a, b; 1939).

London based his considerations on the usual expression for the mean occupation numbers \bar{n}_i , and Fowler and Jones theirs on the equivalent partition function. It was shown, however, by Schubert (1946, 1947)

that the usual derivations of these expressions completely broke down just at the interesting points, namely those where $T \sim T_\lambda$ and $T < T_\lambda$. Other methods show, luckily, that the condensation really does occur, and that the final results are essentially the same as those given by London and by Fowler and Jones. For instance, the author has proved that for a non-degenerate* assembly of non-interacting Bose-Einstein particles, the occupation numbers are exactly given by (Dingle 1949 a) :

$$Z \bar{n}_i = z_i^N \left\{ N - \sum_{p \neq i} \frac{1}{(z_i/z_p) - 1} \right\} \prod_{r \neq i} \left(1 - \frac{z_r}{z_i} \right)^{-1} \\ + z_i \sum_{s \neq i} \frac{z_s^{N-1}}{1 - (z_i/z_s)} \prod_{r \neq s} \left(1 - \frac{z_r}{z_s} \right)^{-1} \quad . \quad . \quad (43)$$

where Z is the partition function

$$Z = \sum_s z_s^N \prod_{r \neq s} (1 - z_r/z_s)^{-1} \quad . \quad . \quad . \quad (44)$$

and $z_i = \exp(-E_i/kT)$. Let the lowest state be labelled z_0 , with $E_0 = 0$ and thus $z_0 = 1$. It is shown in the Appendix to this article that if

$$N - \sum_{p \neq 0} 1/(z_p^{-1} - 1) > 0, \quad . \quad . \quad . \quad (45)$$

the terms involving z_i^{N-1} are negligibly small if N is large. Then (43) and (44) yield

$$\bar{n}_{i \neq 0} = \frac{1}{z_i^{-1} - 1} = \frac{1}{\exp(E_i/kT) - 1}, \quad . \quad . \quad . \quad (46)$$

$$\bar{n}_0 = N - \sum_{p \neq 0} \frac{1}{z_p^{-1} - 1} = N - \sum_{p \neq 0} \frac{1}{\exp(E_p/kT) - 1}, \quad . \quad . \quad . \quad (47)$$

which express the fact that all 'excess particles' within the assembly 'condense' into the lowest state. The squares of the fluctuations from these mean occupation numbers are found to be†

$$\overline{n_{i \neq 0}^2} - (\bar{n}_{i \neq 0})^2 = \frac{z_i^{-1}}{(z_i^{-1} - 1)^2} = \frac{\exp(E_i/kT)}{[\exp(E_i/kT) - 1]^2}, \quad . \quad . \quad . \quad (48)$$

$$\overline{n_0^2} - (\bar{n}_0)^2 = \sum_{p \neq 0} \frac{z_p^{-1}}{(z_p^{-1} - 1)^2} = \sum_{p \neq 0} \frac{\exp(E_p/kT)}{[\exp(E_p/kT) - 1]^2} \quad . \quad . \quad (49) \ddagger$$

* Since we are here interested only in volume effects, this implies no restriction, for any degeneracies could be removed by confining the particles within a rectangular box, the ratios of the sides being incommensurate quantities.

† Since $Z \bar{n}_i^2 = (z_i \partial / \partial z_i)(z_i \partial / \partial z_i) Z = (z_i \partial / \partial z_i)(Z \bar{n}_i)$, the right-hand side of eqn. (6) of Dingle (1949 a) is equal to $Z n_i^2$ and not to $Z(n_i^2 + (\bar{n}_i)^2)$ as there stated.

‡ These fluctuations refer to the values for the whole assembly. If one considers a small volume element within the assembly, one must use the method of the 'grand ensemble'; it is then found that strong *local* fluctuations occur (ter Haar, to be published).

Fraser (1950) has given a detailed and rigorous proof of equivalent results, with special reference to the case of a perfect gas enclosed within a rectangular box. His papers contain criticisms of the work of Leibfried (1947) and Temperley (1949 b). See also Wergeland and Hove-Storhoug (1943) and Kaempffer (1948).

Assuming the usual distribution function, Osborne (1949) has examined the Bose-Einstein condensation of an ideal gas forming a thin film, and de Groot and ten Seldam (1949), and de Groot, Hooyman and ten Seldam (1950) have examined the condensation for systems of various dimensions and various potential fields.

3.3. LANDAU'S QUANTUM HYDRODYNAMICS

Landau (1941) has attempted to construct a quantum theory of liquids by direct quantization of hydrodynamical variables such as the density, the current and the velocity, without explicit reference to the interatomic forces.

Let R be the radius vector of a point in space, and r_α the radius vector of the centre of gravity of a particle of mass m . Then Landau defines the density of a liquid at a point R to be

$$\rho(R) = \sum_{\alpha} m \delta(r_\alpha - R) \quad (50)$$

where $\delta(r - R)$ is the 3-dimensional delta-function, infinite at $r = R$ but zero elsewhere, and normalized in such a way that its integral over space is unity. The quantity $\rho(R)$ refers to the local density, and not to the customary smoothed value. Its integral over all space is, of course, equal to the total mass of the assembly. Classically, if dV represents a volume element,

$$\int \rho dV = m \sum_{\alpha} \int \delta(r_\alpha - R) dV = m \sum_{\alpha} 1 = \text{total mass} \quad . . . (51)$$

Quantally, the expectation value of the density is, in a one-particle system,

$$\overline{\rho(R)} = \int \psi^*(r) \rho(R) \psi(r) dV = m \int \psi^*(r) \delta(r_\alpha - R) \psi(r) dV = m \psi^*(R) \psi(R) \quad . . . (52)$$

as expected.

The current at the point R , i.e. the number of particles crossing unit area per unit time, is defined by Landau by the expression

$$j(R) = \frac{1}{2} \sum_{\alpha} (p_\alpha \delta(r_\alpha - R) + \delta(r_\alpha - R) p_\alpha), \quad (53)$$

where p_α is the momentum of the particle labelled α ; the mean value of the sum of $p_\alpha \delta$ and δp_α being taken to ensure that the current is always a real quantity, as it must be on physical grounds. Assuming that the relation $p_\alpha = -i\hbar \text{grad}_\alpha$ may be taken over from quantum mechanics, it is easily shown that the expectation value of the current is, for a one-particle system,

$$\overline{j(R)} = \frac{1}{2} i\hbar (\psi \text{ grad } \psi^* - \psi^* \text{ grad } \psi) \quad (54)$$

as expected.

Landau also introduces a velocity operator related to the current at the point by the expressions

$$j = \frac{1}{2}(\rho v + v \rho); \quad v = \frac{1}{2} \left(\frac{1}{\rho} j + j \frac{1}{\rho} \right). \quad (55)$$

Finally the Hamiltonian of the total assembly is assumed to be

$$\mathcal{H} = \int \left\{ \frac{1}{2} v \rho v + \rho U(\rho) \right\} dV, \quad (56)$$

the term $\frac{1}{2} v \rho v$ in the integrand representing the kinetic energy, and the term $U(\rho)$ the ordinary internal energy per unit mass. The time rate of change $\partial f / \partial t$ of any operator f is taken from quantum mechanics to be given by

$$i\hbar \partial f / \partial t = f \mathcal{H} - \mathcal{H} f. \quad (57)$$

In deriving the commutation relations between ρ , j , v , \mathcal{H} , and their derivatives, it is assumed that operators corresponding to different particles commute. Landau shows that the components of $\text{curl } v$ do not commute with one another, i.e.

$$(\text{curl } v)_i (\text{curl } v)_j - (\text{curl } v)_j (\text{curl } v)_i \neq 0, \quad (58)$$

and compares this relation with that for the components of angular momentum M_i , M_j , and M_k , in ordinary quantum mechanics. It is known that for these

$$M_i M_j - M_j M_i = i\hbar M_k, \quad (59)$$

and that since the left-hand side is quadratic in M and the right hand side linear, the angular momentum must be quantized. Landau assumes by analogy that vortex motion is quantized, and that there are thus no states for which $\text{curl } v$ is non-vanishing but is arbitrarily small over the whole volume of the liquid.

In addition to this vortex motion for which $\text{curl } v \neq 0$, there will also be potential motion* for which $\text{curl } v = 0$. Now

$$i\hbar \frac{\partial}{\partial t} (\text{curl } v) = (\text{curl } v) \cdot \mathcal{H} - \mathcal{H} \cdot (\text{curl } v) \quad (60)$$

obviously vanishes if $\text{curl } v = 0$, so that Lagrange's theorem, that *if at a certain time the motion is potential throughout the liquid, it will always be potential*, holds also in Landau's quantum hydrodynamics.

The energy spectra for potential and for vortex motion may thus be considered separately. For the existence of superfluidity (flow with zero viscosity, i.e. flow for which $\text{curl } v = 0$), it is essential that the ground level for potential motion should lie *below* the ground level for vortex motion. The magnitude of the energy gap Δ can depend only on m , ρ , and \hbar , and dimensional analysis then shows that†

$$\Delta \sim \rho^{2/3} \hbar^2 m^{-5/3}, \quad (61)$$

corresponding to an excitation temperature Δ/k of the order of a few degrees for liquid helium.

* i.e. motion in which the velocity can be derived from a potential.

† Landau gives $\Delta \sim m^{5/1} \rho^2 \hbar^2$, but this seems to be due to a printing error.

3.31. Roton Spectrum

If energies are measured on a scale in which the ground state of potential motion is reckoned as zero, the energy of an excitation of the vortex spectrum, which excitation Landau calls a 'roton', must be related to its momentum p by an expression of the form

$$E(p) = \Delta + f(|p|) \quad . \quad . \quad . \quad . \quad . \quad (62)$$

since the liquid is isotropic. Without a detailed knowledge of the energy levels of the vortex spectrum, it is impossible to determine the function f , and some further assumption becomes necessary. If the rotons move through the liquid as quasi-free particles, we are led to Landau's original postulate (1941) that

$$E(p) = \Delta + p^2/2\mu, \quad . \quad . \quad . \quad . \quad . \quad (63)$$

where μ is the effective mass of a roton (compare § 3.222, eqn. (35)). Since the number of rotons is not prescribed, the degeneracy parameter ξ is equal to unity, and the Helmholtz free energy per unit mass of liquid is

$$F = \pm \frac{kT}{\rho} \frac{4\pi}{h^3} \int_0^\infty \ln [1 \mp \exp(-E/kT)] p^2 dp, \quad . \quad . \quad . \quad (64)$$

the upper signs being taken for the case of Bose-Einstein statistics, the lower for Fermi-Dirac. It is not known with certainty which statistics rotons obey (probably Bose-Einstein, as remarked by Landau), but this turns out to be unimportant, since the excitation temperature Δ/k is found to be of the order $8-9^\circ \text{K}$ and thus considerably greater than the temperatures with which we are concerned. Thus $\exp(-E/kT) \ll 1$, and both versions of (64) reduce to the classical form

$$F_{\text{rot}} = - \frac{kT}{\rho} \frac{4\pi}{h^3} \int_0^\infty \exp(-E/kT) p^2 dp = - \frac{kT}{\rho h^3} (2\pi\mu kT)^{3/2} \exp(-\Delta/kT), \quad . \quad . \quad . \quad (65)$$

whence

$$S_{\text{rot}} = - \left(\frac{\partial F_{\text{rot}}}{\partial T} \right)_e = \frac{k}{\rho h^3} (2\pi\mu kT)^{3/2} \exp(-\Delta/kT) \left\{ \frac{5}{2} + \frac{\Delta}{kT} \right\}, \quad . \quad . \quad . \quad (66)$$

$$C_{\text{rot}} = \left(\frac{T \partial S_{\text{rot}}}{\partial T} \right)_e = \frac{k}{\rho h^3} (2\pi\mu kT)^{3/2} \exp(-\Delta/kT) \left\{ \frac{15}{4} + \frac{3\Delta}{kT} + \left(\frac{\Delta}{kT} \right)^2 \right\}, \quad (67)$$

and $N_{\text{rot}} = -F_{\text{rot}}/kT$, all these quantities being measured per unit mass of liquid.*

In addition to these roton contributions, there are also the phonon contributions given by (42). These phonon contributions will dominate at very low temperatures, since the roton contributions decrease rapidly (exponentially) as the temperature is lowered.

By comparing C_{rot} with the measurements of Keesom and Keesom (1936) (subtracting first the phonon specific heat), Landau concluded that $\Delta/k \sim 8-9^\circ \text{K}$, and $\mu/m_{\text{He}} \sim 7-8$.

* If the rotons obey Bose-Einstein statistics, the exact expressions are just those of § 3.222. If they obey Fermi-Dirac statistics, the only difference is that negative signs must be introduced into alternate terms of (40).

The only feature of the energy spectrum actually derived from the theory is the existence of some energy gap Δ , but the theory does not seem to shed any light on the problem of why its magnitude for liquid ${}^4\text{He}$ is large and positive—as it must be to prevent the number of rotons being so large that T_λ is virtually zero—while that for ${}^3\text{He}$ is (presumably) very small (or else possibly actually negative)—so that there are always sufficient rotons to make $T_\lambda \simeq 0^\circ \text{K}$.

Finally, it is not clear why the energy of rotons arises solely from translational motion, as the form of Landau's energy spectrum would imply. This is important, since if the excitations possessed any rotational energy, the formula for the velocity of second sound would require modification (§ 4.21).

3.4. GREEN'S THEORY OF QUANTUM LIQUIDS

3.41. *Classical Formulation*

In the kinetic theory of gases, one traces the history of a single particle ; the distribution function concerned may therefore be written $f_1(t, x^{(1)}, v^{(1)})$, where the subscript in f_1 refers to a function depending only on one particle, t to the time, and $x^{(1)}$ and $v^{(1)}$ respectively to the position and velocity of the particle. On the other hand, in the ordinary theory of statistical mechanics, one is concerned with all the particles in an assembly, and the distribution function may be written

$$f_N(x^{(1)}, x^{(2)}, \dots, x^{(N)}; v^{(1)}, v^{(2)}, \dots, v^{(N)}),$$

the subscript N referring to the N particles forming the assembly, and $x^{(1)}$ and $v^{(1)}$ respectively to the position and velocity of a typical particle labelled (1), and so on. The time does not appear in this function since statistical mechanics is concerned only with assemblies in equilibrium.

An important advance was made by Born and Green (1946, 1947 a, b; Green 1947, 1948), following work of a similar nature by Kirkwood (1946).^{*} In the classical approximation, Born and Green introduced distribution functions of the form $f_h(t; x^{(1)}, \dots, x^{(h)}; v^{(1)}, \dots, v^{(h)})$ involving h of the N particles forming the assembly. They considered the continuity and dynamical equations obeyed by each function, and the recurrence relations between consecutive functions, f_h and f_{h+1} for instance.

In order to derive explicit results without undue labour, it was found to be necessary to make some additional assumption concerning the relationship between consecutive functions. In the approximation of gas-kinetic theory, it suffices to take

$$f_2^{(1, 2)} = f_1^{(1)} f_1^{(2)}, \dots \dots \dots (69)$$

which simply means that the probability of finding two particles with coordinates $(x^{(1)}, v^{(1)})$ and $(x^{(1)}, v^{(2)})$ is equal to the product of the

^{*} For a summary of the relationship of Born and Green's theory to other work, see Wyllie (1950).

probabilities of finding one particle with coordinates $(x^{(1)}, v^{(1)})$ and another with coordinates $(x^{(2)}, v^{(2)})$; this relation is clearly exact if the particles are independent—i.e. if there is no interaction.

In the application to liquids, Born and Green take

$$f_3^{(1, 2, 3)} = \frac{f_2^{(2, 3)} f_2^{(3, 1)} f_2^{(1, 2)}}{f_1^{(1)} f_1^{(2)} f_1^{(3)}} \quad . \quad . \quad . \quad . \quad (70)$$

Written in the form

$$\frac{f_3^{(1, 2, 3)}}{f_1^{(3)} f_2^{(1, 2)}} = \frac{f_2^{(3, 1)}}{f_1^{(3)} f_1^{(1)}} \times \frac{f_2^{(3, 2)}}{f_1^{(3)} f_1^{(2)}}, \quad . \quad . \quad . \quad . \quad (71)$$

this is seen to imply that the relative probability of finding a particle labelled (3) together with two others is equal to the product of the relative probabilities of particle (3) being found together with each of the other particles considered separately. This approximation relating f_3 , f_2 , and f_1 , will certainly be more accurate than (69) relating only f_2 and f_1 , but whether it suffices for actual liquids is another matter. In this connection, Rushbrooke and Scoins (1951) have shown that it gives correct results for the equation of state only up to, and including, the third virial coefficient.

3.42. *Quantal Formulation*

Born and Green effect a quantization by replacing the classical distribution functions f_h by the corresponding quantum density matrices ρ_h of von Neumann, Dirac and Husimi. They obtain a set of hydrodynamical equations which do not differ in actual form from the corresponding equations of classical hydrodynamics. However, the interpretation of these equations is not the same in that

(1) the temperature defined by the mean kinetic energy of the particles is not identical with that defined as the integrating factor in the equation $dQ = T \cdot dS$, where S is the entropy.

(2) The kinetic pressure defined by the relation $P_{\text{kin}} = -(\partial F / \partial V)_T$, where F is the Helmholtz free energy, is not identical with the thermodynamic pressure defined by the relation $P_{\text{therm}} dV = \text{work done when liquid is displaced}$ (but see § 3.44).

3.43. *Lambda-point*

Since ^4He obeys Bose-Einstein statistics, the wave-function of the assembly must be a symmetrical function of all the atoms. If the coordinates of two particles are interchanged, the wave-function must therefore remain unchanged in magnitude and sign. Thus the relative angular momentum of two particles measured in units of \hbar , l say, must be an even number, i.e. $l = 0, 2, 4, \dots$. Green (1948) finds that at very low temperatures the wave-function corresponding to $l = 0$ appears to be the only one satisfying the boundary conditions for a liquid. The radial distribution function then obtained has the curious property that

it possesses a minimum,* instead of the usual maximum, near the minimum of the interatomic potential. It is supposed that the transition is located at that temperature for which the state of angular momentum $l=0$ begins to be replaced by that for which $l=2$. In a sense, this explanation of the existence of He II is similar to that suggested by Landau, for in his theory if there were always a sufficient number of rotons to 'use up' all the available atoms, there would be no lambda-point. Thus according to Landau, the curious properties of He II are to be correlated with the insufficiency of quantized vortex (rotational) states, whilst according to Green they are to be correlated with the insufficiency of quantized states with non-zero relative angular momenta.

In Green's theory the lambda-temperature is given by

$$kT_i \cong 2h^2/mr^2, \quad (72)$$

where r is the interatomic distance for which the potential energy has its minimum. For liquid helium, $r=2.93 \times 10^{-8}$ cm, giving $T_A=2.28^\circ$ K. Green claims that below this temperature $P_{\text{therm}} \neq P_{\text{kin}}$, and the thermal energy and energy of macroscopic motion can then no longer be considered as independent variables. The consequence of this is that the first law of thermodynamics takes different forms depending on whether the liquid is stationary, in steady motion, or undergoing periodic displacements. The latter case leads to the possibility of the excitation of thermal waves which transfer heat energy and liquid bulk in opposite directions; to these are ascribed the anomalous specific heat of He II, and the negative coefficient of thermal expansion below the lambda-point.

3.44. Comments on Green's Theory

If the curious properties of ${}^4_2\text{He}$ are to be ascribed to the difference between P_{kin} and P_{therm} in a quantum liquid, one may ask why ${}^3_2\text{He}$ should not show similar properties below some transition temperature. It is true that the difference in statistics does enter into Green's theory, the relative angular momentum for Fermi-Dirac particles such as ${}^3_2\text{He}$ being confined to *odd* multiples of \hbar , that for Bose-Einstein particles such as ${}^4_2\text{He}$ to *even* multiples, but one might nevertheless expect the predicted values of T_λ to be of comparable orders of magnitude for similar interatomic forces. A specific calculation for ${}^3_2\text{He}$ would clearly be of interest.

The correctness of Green's conclusion that $P_{\text{kin}} \neq P_{\text{therm}}$ in a quantum liquid has itself been challenged. The question is a difficult one, the existence or non-existence of a difference between the two pressures apparently depending on the nature of the boundary conditions assumed to hold in a liquid. See Yvon (1948); de Boer (1949), Green (1949); Riddell and Uhlenbeck (1950), Green (1950); Horowitz (1950); Price (1950). Also Massignon (1949, 1951) and Gurov (1948, 1950).

* This might only be a point of inflection (P. Hughes, unpublished).

For a possible connection between these theories of quantum liquids and the two-fluid model of He II, see Penrose (1951).

3.5. OTHER THEORIES OF THE PROPERTIES OF He II

Daunt and Mendelssohn (1942) and Mendelssohn (1945, 1951) have stressed the analogy between the phenomena of superfluidity in He II and of superconductivity, and suggest that both are due to a new state of aggregation composed of 'z-particles' (see also Band 1946). They also suggest that transfer by the He film is due to the 'zero-point momentum' of these z-particles (Mendelssohn 1945, 1948; Daunt and Mendelssohn 1946).

Rice (1949, 1950) has suggested that there is some reason to suppose that the two fluids of He II are separated not only in momentum space, as in F. London's theory, but also in ordinary space, and cites in evidence Taconis' assumption that ^3He dissolves only in the normal part of ^4He II.* In this connection, see also the work of Becker (1950) and Leibfried (1950) on the condensation of Bose-Einstein gases as a space phenomenon.

Macleod and Yeabsley (1946) have put forward the theory that He II is a mixture of ordinary He I and the intermediate form of a fluid indicated by van der Waals' equation. They claim to show that the intermediate form is possible below a certain temperature, which they identify with the lambda-point of helium.

Benedicks (1947) has suggested that the properties of He II may be explained in terms of an allotropic transformation at the lambda-point arising from the ionization of the He atoms by frictional electricity at the walls of the vessel.

§4. HYDRODYNAMICS OF He II FOR SMALL VELOCITIES

4.1. BASIC CONCEPTS

At absolute zero, any substance (provided it is stable rather than meta-stable) is in its ground state, and its entropy can be taken as zero. At finite temperatures, its entropy is described by deviations from the configuration corresponding to the ground state. These deviations may be expressed in terms of excitations, such as phonons (Debye waves; (42), § 3.23), rotons (quantized vortex motion, § 3.31), or simply excited atoms moving in a self-consistent field (§ 3.22). Since we are concerned only with a system of one component, He atoms, all thermodynamic functions contributed by the various excitations—such as their entropies, the contributions of the various excitations to the entropy, the number

* Taconis, Beenakker, Nier and Aldrich (1949) made this suggestion in an attempt to explain their experimental result that the effect on the vapour pressure of ^4He II caused by the addition of ^3He is much greater than that predicted by Raoult's law. In this connection, however, it may be noted that according to Eselson, Lasarew and Alekseevski (1950). Raoult's law is obeyed.

of excitations, etc.—must be additive provided the usual statistical distribution functions are valid.*

When the liquid is left undisturbed, the excitations have no preferred direction of movement. When, however, a temperature gradient is introduced, the excitations acquire a drift velocity in such a direction as to tend to nullify the imposed temperature gradient. Since the excitations represent deviations from the configuration of the ground state, the relevant drift velocity, v say, must be measured relative to the ground state configuration.

4.11. Effective Mass

The drift motion of the excitations will correspond to a certain momentum per unit volume, $\rho_n v$ say, where ρ_n is the effective mass-density of the excitations in their motion relative to the configuration of the ground state. An observer drifting along with the excitations (*dashed coordinates*) can apply to them the usual statistical distribution function. Thus for non-interacting excitations

$$\bar{n} \propto \frac{1}{\xi \exp \{ (E'/kT) \mp 1 \}} \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (73)$$

It is necessary to find how this statistical relation is modified according to an observer moving with the ground state configuration (*undashed coordinates*) i.e. moving at a velocity v relative to the drifting excitations. The wave-function of an excitation may be written†

$$\psi \propto \exp \left\{ \frac{1}{i\hbar} (E't - p \cdot r') \right\}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (74)$$

so that in the undashed coordinate system, ($r=r'+vt'$, $t=t'$),

$$\psi \propto \exp \left\{ \frac{1}{i\hbar} (Et - p \cdot r) \right\}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (75)$$

where

$$E = E' + p \cdot v. \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (76)$$

Thus by (73), according to the observer moving with the ground state configuration,

$$\bar{n} \propto \frac{1}{\xi \exp \{ (E - p \cdot v)/kT \} \mp 1} \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (77)$$

* The types of excitations are indeed *chosen* so that the usual statistical distribution functions are valid, i.e. the excitations must be approximately equivalent to the normal modes of the assembly studied. If they are not so chosen, it is very difficult to proceed with the theory. Gorter's (1949) attempt to generalize the equations of hydrodynamics of He II to cover cases where entropies are not additive, does not seem to me to be correct (Dingle 1951). Bogolyubov (1947, 1948) has attempted to calculate the corrections to the distribution function necessary when there are interactions. He uses an ingenious method akin to second quantization.

† Witness the usual quantal relations $p\psi \equiv -i\hbar \text{grad}' \psi$ and $E'\psi \equiv i\hbar \partial\psi/\partial t'$.

We shall see in § 5 that terms in v correspond to work which must be done on the assembly in order to increase the relative drift velocity of the excitations from 0 to v .

[Instead of regarding E' as the energy of the excitation itself, it may be regarded as the energy of the assembly in which the excitation has appeared. The relation $E=E'+p \cdot v$, where p is now interpreted as the momentum of the assembly of mass M , may then be derived as follows :

	In dashed coordinates	In undashed coordinates
Velocity*	V'	$V=V'+v$
Kinetic energy	$\frac{1}{2}M(V')^2$	$\frac{1}{2}M(V')^2=\frac{1}{2}MV^2+\frac{1}{2}Mv^2-MvV$
Potential energy	U	U
Lagrangian, L .	$\frac{1}{2}M(V')^2-U$	$\frac{1}{2}MV^2+\frac{1}{2}Mv^2-MvV-U$
Momentum	$p'=\partial L/\partial V'=MV'$	$p=\partial L/\partial V=MV-Mv=MV'=p'$
Apparent energy (Hamiltonian)	$E'=p'V'-L$ $=(p')^2/2m+U$	$E=pV-L$ $=p^2/2m+p \cdot v+U$ $=E'+p \cdot v$

* A 'virtual' velocity V' has been assumed because this method of derivation requires a differentiation with respect to it.

By a similar argument, it may be shown (cf. Landau and Lifshitz 1938, § 19) that if the excitations have a drift *angular* momentum Ω with respect to the ground state configuration, $E=E'+\Omega \cdot \omega$, where ω is their drift angular velocity.]

The drift linear momentum of the excitations relative to the ground state configuration is

$$\rho_n v = \frac{1}{h^3} \int_0^\infty p^2 dp \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi \frac{p \cos \theta}{\xi \exp \{(E - pv \cos \theta)/kT\} \mp 1}, \quad (78)$$

where θ is the angle between p and v . Neglecting terms of order v^2 , we have

$$\rho_n = -\frac{4\pi}{3h^3} \int p^4 dp \frac{\partial}{\partial E} \left(\frac{1}{\xi \exp (E/kT) \mp 1} \right). \quad (79)$$

Virtually this equation is due to Landau (1941), though he did not give it in this explicit general form.† The quantity ρ_n includes the material mass which is capable of movement ; for instance, in a perfect Fermi–Dirac gas, or in a perfect Bose–Einstein gas above its ‘condensation’

† Temperley (private communication) has recently derived a relation equivalent to (79) by introducing into the usual derivation of the distribution function an additional selector variable for the momentum.

Tisza (1947) and Nakajima and Shimizu (1950), have attempted to prove that $\rho_n \propto S$, whilst Gorter (1949) has implicitly assumed in his theory that $\rho_n \propto N_n$ (see also Temperley 1951 a). I have criticized these interpretations in a recent paper (Dingle 1951).

temperature, ρ_n is equal to ρ ; in a perfect Bose-Einstein gas below its condensation temperature, $\rho_n/\rho = N_n/N$. It also includes any non-material effective mass, such as that associated with phonons.

4.12. Assumption of Local Equilibrium*

This calculation of the effective mass-density, and the corresponding calculations for the thermodynamical quantities F , U and S , are valid only on the assumption that local equilibrium is attained within a distance much smaller than that in which there is an appreciable fractional change in ρ , F , U , S or T . For instance, in the propagation of second sound of wavelength λ , the calculations are valid only if

$$\lambda \gg l, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (80)$$

where l is the mean free path of the excitations (cf. London 1951, Ward and Wilks 1952).† If this condition were not satisfied, the theory would have to be reformulated in terms of a kinetic theory for a non-uniform gas of excitations. It is probable that second sound could not be propagated at all in the complete absence of local equilibrium, i.e. if $\lambda \ll l$. Theory also indicates the possibility that under some circumstances more than one type of second sound might exist; this could occur, for example, if more than one type of excitation were possible, local equilibrium being attained within each type, but not between the types.

4.13. Andronikashvili Experiment

The quantity ρ_n/ρ is equal to the fractional effective mass of liquid helium carried round with the vanes in the experiments of Andronikashvili (1946, 1948 a) and Hollis-Hallett (1950, 1952) described in § 1.3.

[Temperley (1951 a) has made the interesting suggestion that for some models the 'linear' and 'rotational' calculations of ρ_n/ρ might differ, because in the rotational case some excited states correspond to zero angular momentum. In my opinion this difference can never be significant, since the number of such excited states depends on the number of combinations of the possible values of only *two* quantum numbers—the third (rotational) quantum number being zero—and must therefore be negligible in comparison with the total number of excited states, which depends on the number of combinations of the possible values of all *three* quantum numbers.]

4.14. Equations of Continuity

We define the current j to be the momentum, as reckoned by a stationary observer, per unit volume of liquid. According to an observer moving along with the ground state configuration (superfluid in the case of He II), the momentum is that of the excitations moving past him, $\rho_n v$.

* See also the further assumptions noted in § 4.8.

† A similar assumption of quasi-equilibrium within a 'sub-assembly' is required in the theory of the thermal conductivity of solids (Peierls 1929).

On ceasing to move along with the ground state configuration, the observer, now stationary, would see the entire liquid moving past him with velocity v_s , where v_s is the velocity of the ground state configuration. Hence, according to a stationary observer, the current is

$$j = \rho_n v + \rho v_s = \rho_n v_n + \rho_s v_s, \quad \dots \quad (81)$$

where we write $v = v_n - v_s$; here v_n is the drift velocity of the excitations (the 'normal fluid' of He II) and v_s the velocity of the 'superfluid', both as reckoned by a stationary observer; $\rho_s = \rho - \rho_n$ is the effective mass of the 'non-excitations'. By the law of conservation of mass

$$\partial \rho / \partial t + \text{div } j = 0, \quad \dots \quad (82)^*$$

By an argument similar to that leading to (81), the entropy current per unit volume is, according to a stationary observer,

$$(\rho S)v + (\rho S)v_s = \rho S v_n, \quad \dots \quad (83)$$

where $S = S(v^2)$ is the entropy per unit mass. Then by the law of conservation of entropy valid for reversible processes,

$$\partial(\rho S) / \partial t + \text{div } (\rho S v_n) = 0, \quad \dots \quad (84)$$

for we shall see in § 5 that the 'static' and 'dynamic' entropies are identical. This equation was first introduced into the theory by Landau (1941). A similar equation is introduced into the theory of supersonic flow and shock waves (e.g. Courant and Friedrichs 1948).

4.2. VELOCITIES OF FIRST AND SECOND SOUND

When the velocities v_n and v_s are small (acoustic approximation), we may ignore terms of order v_n^2 and of order v_s^2 in the hydrodynamical equations. The continuity equations, here expressed in terms of displacements x_n and x_s rather than of velocities v_n and v_s , are

$$\delta \rho + \text{div } (\rho_n x_n + \rho_s x_s) = 0, \quad \dots \quad (85)$$

$$\delta(\rho S) + \text{div } (\rho S x_n) = 0, \quad \dots \quad (86)$$

The increase in potential energy per unit mass when the volume and entropy are increased by δV and δS respectively is given by the second order terms in the Taylor expansion of δU , i.e. by

$$\begin{aligned} \frac{1}{2} \left(\frac{\partial^2 U}{\partial V^2} \right) (\delta V)^2 + \left(\frac{\partial^2 U}{\partial V \partial S} \right) \delta V \cdot \delta S + \frac{1}{2} \left(\frac{\partial^2 U}{\partial S^2} \right) (\delta S)^2 &= \frac{1}{2} \left(\frac{\partial \rho}{\partial \rho} \right)_s \left(\frac{\delta \rho}{\rho} \right)^2 \\ &+ \frac{\alpha}{\rho} \left(\frac{\partial \rho}{\partial \rho} \right)_T \frac{T}{C_v} \delta \rho \cdot \delta S + \frac{1}{2} \frac{T S^2}{C_v} \left(\frac{\delta S}{S} \right)^2, \quad \dots \quad (87)^\dagger \end{aligned}$$

* Whether this equation and the following ones still remain valid when ρ_n varies with v^2 is a matter requiring further investigation. Only terms involving cubes and higher powers of the velocities could be affected, because ρ_n always appears in conjunction with a velocity.

† The introduction of this expression into the theory is due to Tisza (1947). The actual equations of motion may be found from this potential energy. They are identical with those given in § 5 omitting terms of order v_n^2 and of order v_s^2 (Dingle 1949 d).

where α is the coefficient of thermal expansion. Eqn. (87) is, in fact, the expression needed to calculate fluctuations in the thermodynamical quantities (Landau and Lifshitz 1938).

The corresponding kinetic energy per unit mass is

$$\frac{1}{\rho} \left\{ \frac{1}{2} \rho_n \dot{x}_n^2 + \frac{1}{2} \rho_s \dot{x}_s^2 \right\}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (88)$$

where dots denote differentiation with respect to time.

The coefficient of thermal expansion is very small for He II ($\alpha \sim -3 \times 10^{-3} \text{ deg}^{-1}$), and may be neglected for most purposes. In this approximation the suffixes in (87) may also be omitted. The potential energy divides into two squared terms, the first corresponding to density fluctuations giving rise to ordinary first sound (pressure waves), the second to entropy fluctuations giving rise to second sound (temperature waves).*

In first sound, $\delta S = 0$, and the consistency of (85) and (86) requires that $x_n = x_s = x$ say. *The normal fluid and superfluid therefore move together during the propagation of first sound.* Thus we have, per unit mass,

$$\text{potential energy} = \frac{1}{2} \frac{\partial p}{\partial \rho} \left(\frac{\delta \rho}{\rho} \right)^2 = \frac{1}{2} \frac{\partial p}{\partial \rho} (\text{div } x)^2; \text{ kinetic energy} = \frac{1}{2} \dot{x}^2, \quad . \quad . \quad . \quad (89)$$

leading to a velocity of propagation c given by the customary value

$$c^2 = \partial p / \partial \rho. \quad . \quad . \quad . \quad . \quad . \quad . \quad (90)$$

In second sound, $\delta \rho = 0$. By (85), this leads to the relation

$$\rho_n x_n + \rho_s x_s = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad (91)$$

showing that *the centre of gravity of the normal fluid and superfluid remains at rest in second sound.* Thus we have, per unit mass,

$$\text{potential energy} = \frac{1}{2} \frac{TS^2}{C} \left(\frac{\delta S}{S} \right)^2 = \frac{1}{2} \frac{TS^2}{C} (\text{div } x_n)^2; \text{ kinetic energy} = \frac{1}{2} \rho_n \dot{x}_n^2 / \rho_s, \quad . \quad . \quad . \quad (92)$$

leading to a velocity of propagation c_2 given by

$$c_2^2 = \frac{\rho_s}{\rho_n} \frac{TS^2}{C}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (93)$$

It should be remembered that S and C are taken per unit mass.

If $\alpha \neq 0$, there is a coupling between first and second sound—i.e. the density and pressure fluctuations characteristic of first sound give rise to small entropy and temperature fluctuations, while conversely the fluctuations in entropy and temperature characteristic of second sound give rise to small density and pressure fluctuations. This coupling has

* Agarwala and Chowdri (1947) have made the interesting suggestion that the Rayleigh line in the spectrum of light scattered by He II should consist of four lines, rather than the two characteristic of ordinary liquids. For in He II both density and entropy fluctuations can move, whilst in ordinary liquids only density fluctuations are capable of movement.

been investigated theoretically by Lifshitz (1944), Peshkov (1948a), and the writer (Dingle 1950). As far as the effect on the actual velocities of propagation is concerned, it is found that (Dingle 1950)

$$c^2 = c_s^2 + \frac{c_{20}^2(c_s^2 - c_T^2)}{c_s^2 - c_{20}^2} = c_T^2 + \frac{c_s^2(c_s^2 - c_T^2)}{c_s^2 - c_{20}^2}, \quad \dots \quad (94)$$

$$c_{20}^2 = c_{20}^2 \left\{ 1 - \frac{c_s^2 - c_T^2}{c_s^2 - c_{20}^2} \right\} = c_{20}^2 \left\{ \frac{c_T^2 - c_{20}^2}{c_s^2 - c_{20}^2} \right\}, \quad \dots \quad (95)$$

where

$$c_s^2 = (\partial p / \partial \rho)_S; \quad c_T^2 = (\partial p / \partial \rho)_T; \quad c_{20}^2 = TS^2 \rho_s / C \rho_n. \quad \dots \quad (96)$$

4.21. Rotational Energy

It has been implicitly assumed throughout that the energy of the excitations is entirely due to their translational motion, i.e. to their linear momentum. It is possible that some of the excitations possess an additional energy due to angular momentum: for instance, there does not appear to be any obvious reason why rotons should not possess a spin (§ 3.33). If this is so, the formula for the velocity of first sound is unaltered, but it appears that the formula for the velocity of second sound should be modified to

$$c_2^2 = \left(\frac{\rho_s}{\rho_n} \right)_{\text{trans}} \frac{TS_{\text{trans}} S_{\text{total}}}{C_{\text{total}}}. \quad \dots \quad (97)$$

4.3. VELOCITY OF SECOND SOUND AS A FUNCTION OF TEMPERATURE

The effective mass-density of the excitations is given by (79) as

$$\rho_n = - \frac{4\pi}{3\hbar^3} \int p^4 dp \cdot \frac{\partial}{\partial E} \left(\frac{1}{\xi \exp(E/kT) \mp 1} \right). \quad \dots \quad (98)$$

We now calculate the contributions to ρ_n , and the consequent value of c_2 , from the various types of excitations discussed in § 3.

4.31. Velocity in a Phonon Gas

In a phonon gas, $E(p) = pc$,* where c is the velocity of ordinary sound, and the degeneracy parameter ξ is equal to unity since the number of phonons is not prescribed. On integrating by parts, (98) then leads to

$$\left(\frac{\rho_n}{\rho} \right)_{\text{phon}} = \frac{4}{3} \frac{U_{\text{phon}}}{c^2}, \quad \dots \quad (99)$$

where U_{phon} is the internal energy per unit mass of the liquid. We have then

$$C = aT^3; \quad S = \int C dT/T = \frac{1}{3}aT^3; \quad U = \int C dT = \frac{1}{4}aT^4; \quad \rho_n/\rho = \frac{1}{3}aT^4/c^2, \quad (100)$$

* since all phonons move with the velocity $c = \partial E(p) / \partial p$ independent of momentum $= \hbar$ wavelength. The phonon model is practically equivalent to the assumption that the potential energy is proportional to the sum of the squares of the displacements of the particles from their mean positions (e.g. Peierls 1929).

where, by (42), $a=16\pi^5k^4/15\rho h^3c^3$. The velocity of second sound assuming only phonon excitations is therefore

$$c_2 = \frac{c}{\sqrt{3}} \left(1 - \frac{1}{3} \frac{aT^4}{c^2} \right)^{1/2} \dots \dots \dots (101)$$

The velocity of first sound c has been measured by Findlay *et al.* (1938, 1939), Pellam and Squire (1947), and Atkins and Chase (1951). Atkins and Chase estimate that c tends to 237 m/s as T tends to 0, so that $c/\sqrt{3} \rightarrow 137$ m/s. Atkins and Osborne (1950) give, as their result of a direct measurement of the velocity of second sound at about 0.1°K , the value $c_2=152$ m/s, and thus in only moderate agreement with the expected limit $c_2 \rightarrow c/\sqrt{3}$. It is my belief, however, that there is a considerable correction to be applied to Atkins and Osborne's values of c_2 at very low temperatures, a correction arising from ordinary viscous absorption. These authors took the time of arrival of the distorted pulse to be that corresponding to the *start* of the received signal. But in the propagation of either first or second sound in a viscous medium, the distorted pulse begins to arrive *before* it would if the medium were non-viscous, so that Atkins and Osborne must have overestimated the true velocity. The correction to be applied to Atkins and Osborne's results is thus in the right direction to bring about agreement between $c/\sqrt{3}$ and c_2 , and is, in fact, of about the right magnitude if the viscosity (at the very high frequency concerned) is taken to be of the same order as that measured at 1.5°K (Dingle, to be published).

[Atkins and Chase (1951) suggested that the apparent discrepancy between c_2 and $c/\sqrt{3}$ might be caused by dispersion of first sound, the value of c measured at 1.4×10^7 c/s being inserted into the formula instead of its value at the important phonon frequencies around kT/h , about 2×10^9 c/s at 0.1°K . This hypothesis no longer seems to be tenable, for Kramers (1951) has recently measured the specific heat directly and finds that below 0.6°K , $C=8.5 \times 10^{-4} T^3 \text{ cal cm}^{-3} \text{ deg}^{-1}$, which by (42) corresponds to an actual phonon velocity of $c=225$ m/s, so that $c/\sqrt{3}=130$ m/s, in even worse agreement with Atkins and Osborne's stated value of $c_2 \rightarrow 152$ m/s. As far as it goes, the evidence is that the dispersion is in the opposite direction to that required by Atkins and Chase to explain the apparent discrepancy between c_2 and $c/\sqrt{3}$.]

Above about 0.3°K the velocity c_2 drops rapidly with temperature, suggesting that some other type of excitation now provides the predominant contribution to ρ_n . On the other hand, these new excitations do not appear to give rise to a marked change in C and S until a temperature of about 0.6°K (Kramers 1951). These results are not necessarily in conflict, since the relations between C , S and ρ_n and the temperature depend on the nature of the excitations, so that at a given temperature the contributions from one type of excitation may predominate in ρ_n , but not in C or in S . It is also possible (Temperley, private communication) that dispersion of ordinary first sound is responsible for at least part of the difference.

4.311. *Theories of Ward and Wilks.*—Ward and Wilks (1951, 1952) have given two ingenious evaluations of c_2 specifically for a phonon gas model. The first is based on Curtis' (1950) value $(\partial P/\partial \rho)^{1/2}$ for the velocity of sound in general relativity, P being the pressure and ρ the mass-energy density. Since in a phonon gas $C=\alpha VT^3$, the free energy $F=-\alpha VT^4/12$, and thus $P=-(\partial F/\partial V)_T=\alpha T^4/12=\frac{1}{3}u$, where $u=U/V$ is the phonon energy density. Ward and Wilks put $u=\rho_{\text{phon}}c^2$, so that $P=\frac{1}{3}\rho_{\text{phon}}c^2$, and hence they find

$$c_2=(\partial P/\partial \rho_{\text{phon}})^{1/2}=c/\sqrt{3}. \quad (102)$$

Their second evaluation is based on the Boltzmann equation, which for phonons reads

$$\frac{\partial f}{\partial t} + \frac{cp^i}{p} \frac{\partial f}{\partial x^i} = \Delta_{\text{collisions}} f, \quad (103)$$

where $f(x^i, p^i)$ is the phonon distribution function. Multiplying (103) throughout by pc , or by p^k , and integrating over momentum space, Ward and Wilks obtain

$$\frac{\partial U}{\partial t} + c^2 \frac{\partial P^i}{\partial x^i} = 0; \quad \frac{\partial P^i}{\partial t} + \frac{1}{3} \frac{\partial U}{\partial x^i} = 0, \quad (104)$$

since the terms involving $\Delta_{\text{collisions}} f$ vanish on account of the laws of conservation of momentum and energy, and further

$$\int p c f d^3 p = U, \quad \int p^i f d^3 p = P^i \quad \text{and} \quad \int (p^i p^k / p) f d^3 p \simeq \frac{1}{3} \delta^{ik} U / c,$$

provided the distribution function deviates but slightly from spherical symmetry. Eqns. (104) again indicate a velocity of propagation $c_2=c/\sqrt{3}$.*

As regards the first of these derivations, it must be remarked that the relations $u=\rho c^2$ and $c=(\partial P/\partial \rho)^{1/2}$ appear to have been proved only for assemblies composed of a fixed number of material particles, and it is by no means obvious that they can be applied to a non-uniform assembly of phonons not necessarily constant in number. In particular, it is not made clear why one should take the relevant value of ρ to be u/c^2 (Ward and Wilks), rather than, for instance, Landau's value $(\rho_n)_{\text{phon}}=\frac{4}{3}u/c^2$ (eqn. (99)).

In both derivations it is implicitly assumed that the whole assembly can be described in terms of the excitations alone; in particular it is supposed that the assembly in its ground state is incapable of acquiring

* Since this was written, I have used a somewhat similar argument to calculate the velocity of second sound for a general energy spectrum $E=E(p)$. The result is $c_2^2=TS^2\rho/C\rho_n$. The explanation of the discrepancy between this expression and the correct one, $c_2^2=TS^2\rho_s/C\rho_n$, is probably that any description in terms of the excitations alone is adequate only if their effective mass is negligible in comparison to the inertial mass of the total assembly.

kinetic energy. It seems to the author, however, that the *general* admission of such a restriction would lead to four contradictions with experiment :

1. In the Rayleigh disc experiment (Pellam and Morse 1950) there would be no contribution from the kinetic energy of the 'superfluid'.

2. The formula for the velocity of second sound would become $c_2^2 = TS^2\rho/C\rho_n$, and c_2 would thus no longer decrease to zero at the lambda-point.

3. Second sound would be accompanied by considerable fluctuations in pressure, since the drift momentum of the normal fluid would no longer be practically neutralized by the drift momentum of the superfluid.

4. In experiments on shock waves (§ 5.4), back-edge shocks would not be observed near the lambda-point, since α_2 would remain positive if the 'superfluid' could not carry momentum.

4.32. Velocity in a 'Condensed' Bose-Einstein Assembly

For an ideal Bose-Einstein gas, (98) immediately leads to the relation

$$\frac{\rho_n}{\rho} = \frac{N_n}{N} = \left(\frac{T}{T_\lambda}\right)^{3/2} \dots \dots \dots (105)^*$$

The corresponding velocity of second sound is

$$c_2 = \left[\frac{5kT\zeta(5/2)}{3m\zeta(3/2)} \left(1 - \left(\frac{T}{T_\lambda}\right)^{3/2}\right) \right]^{1/2} = 0.925 \left(\frac{kT}{m}\right)^{1/2} \left(1 - \left(\frac{T}{T_\lambda}\right)^{3/2}\right)^{1/2} \quad (106)^\dagger$$

If, on the other hand, each particle moves in a self-consistent field, we may take $E(p) = Ap^{1/r}$ as in § 3.22, and find that

$$\frac{\rho_n}{\rho} = \frac{4\pi r}{3h^3\rho A^{5r}} \Gamma(5r) \cdot \zeta(5r-1) \cdot (kT)^{5r-1}, \quad \dots \dots (107)$$

which we write $\rho_n/\rho = (T/T')^{5r-1}$. With (26) and (27), this gives

$$c_2 = \frac{A^r}{r} (kT)^{1-r} \left[\frac{\Gamma(3r+2) \cdot \zeta(3r+1)}{3 \cdot \Gamma(5r) \cdot \zeta(5r-1)} \left(1 - \left(\frac{T}{T'}\right)^{5r-1}\right) \right]^{1/2} \quad (108)$$

The alternative self-consistent field (§ 3.222)

$$E(p) = \Delta + p^2/2\mu, \quad \dots \dots \dots (109)$$

leads to

$$\frac{\rho_n}{\rho} = \frac{\mu N_n}{\rho V} = \frac{\mu(2\pi\mu kT)^{3/2}}{\rho h^3} \exp(-\Delta/kT) f_{3/2}(T). \quad \dots \dots (110)$$

With (38) and (39), this gives

$$c_2 = \left(\frac{kT}{\mu}\right)^{1/2} \left\{ \frac{5}{2} f_{5/2}(T) + \frac{\Delta}{kT} f_{3/2}(T) \right\} \left\{ 1 - \frac{\mu(2\pi\mu kT)^{3/2}}{\rho h^3} f_{3/2}(T) \exp(-\Delta/kT) \right\}^{1/2} \\ \div f_{3/2}^{1/2}(T) \left\{ \frac{15}{4} f_{5/2}(T) + \frac{3\Delta}{kT} f_{3/2}(T) + \left(\frac{\Delta}{kT}\right)^2 f_{1/2}(T) \right\}^{1/2} \quad \dots \dots (111)$$

* For an ideal Fermi-Dirac gas, $\rho_n = \rho$ since $N_n = N$.

† This assumes that the coefficient of thermal expansion of the total assembly is negligible. For an isolated Bose-Einstein gas, the value of c_2 must be found from (95); it is roughly that given by (106) multiplied by $c_T/c_S = (C_v/C_p)^{1/2} = \gamma^{-1/2}$.

If, as is in fact found for He II, $\Delta \gg kT$, all the f 's are approximately equal to unity.

These formulae (108) and (111) may be made to fit the experimental results adequately for temperatures above about 1.2°K . Below this temperature, it is necessary to add the phonon contributions given by (42), and insert the quantities $\rho_n = (\rho_n)_{BE} + (\rho_n)_{\text{phon}}$, $S = S_{BE} + S_{\text{phon}}$, and $C = C_{BE} + C_{\text{phon}}$ into the expression for c_2 .

It is interesting to note that these formulae involve a characteristic temperature T' defined by the relation $\rho_n(T') = \rho$, as distinct from the lambda-temperature T_λ defined by the relation $N_n(T_\lambda) = N$. Except for a perfect gas, $T' \neq T_\lambda$. Thus, according to this model, the velocity of second sound need not in general vanish precisely at the discontinuity (lambda-point) in the specific heat. There is no experimental evidence for any difference in these characteristic temperatures, and it is probable that the theoretical difference reflects some inadequacy in the model, such as the failure to take proper account of correlations between the positions of the particles. In any case, the whole theory probably breaks down when N_n/N and ρ_n/ρ approach unity, since under such circumstances collisions could lead to a fundamental change in the energy spectrum.

4.33. Velocity in a Roton Gas

The roton spectrum proposed by Landau in 1941 is identical with (109), and the velocity of second sound is therefore given by (111). With the alternative roton spectrum introduced by Landau in 1947,

$$E(p) = \Delta + (p - p_0)^2/2\mu, \quad \dots \dots \dots (112)$$

it is found that

$$c_2 \doteq \frac{3^{1/2}kT}{p_0} \frac{1 + 3kT/\Delta}{\{1 + kT/\Delta + \frac{3}{4}(kT/\Delta)^2\}^{1/2}} \left\{ 1 - \frac{2\mu^{1/2}p_0^4 \exp(-\Delta/kT)}{3(2\pi)^{3/2}\rho(kT)^{1/2}\hbar^3} \right\}^{1/2} \dots \dots (113)$$

provided that $p_0 \gg (2\mu\Delta)^{1/2}$. Again, the phonon contributions must be added for $T \lesssim 1.2^\circ \text{K}$.

4.4. VELOCITY OF SECOND SOUND AS A FUNCTION OF PRESSURE

The manner in which c_2 depends on the external pressure is, of course, determined by the pressure-dependences of S , C , and ρ_n . Neither the theory of Bose-Einstein condensation of a liquid, nor the theory of rotons, is sufficiently developed to make a calculation of such sensitive quantities as pressure dependences really worthwhile* and we record only the experimental fact that at least down to about 1°K , $\partial c_2/\partial p$ is small and negative (Peshkov and Zinovyeva 1948, Maurer and Herlin 1951).

At very low temperatures, where only phonon excitations need be considered, $\partial c_2/\partial p = 3^{-1/2} \partial c/\partial p$, and must therefore be positive, as remarked by Maurer and Herlin (1951).

* The Bose-Einstein theory suggests, for example, that $\partial T_\lambda/\partial p$ is positive, which is contrary to experiment.

4.5. TWO-FLUID MODEL

It will have been seen, particularly from § 4.14, that the theory refers to a *mathematical* and not to a physical separation into terms involving v_n and terms involving v_s . In the first instance this mathematical separation is not even into the so-called 'normal and superfluids', but into the drift motion of excitations relative to the ground state configuration, and the motion of this configuration relative to a stationary observer. Only by a further mathematical transformation do we reach the familiar separation into the 'normal fluid' and the 'superfluid'.

In view of this, the terms 'two-fluid theory' and 'two-fluid model' are, in my opinion, unfortunate, at least as far as concerns theories of the type described above. The significant model is not so much that of two fluids, but that corresponding to the choice of the excitations, and in the supposition that their mutual interactions do not appreciably influence the results, an assumption also made in the usual calculations of thermodynamical quantities. The rest of the theory is concerned with the correlations between the fluctuations in the density in first sound, and in the entropy in second sound.

It seems to me that the opinion sometimes expressed that the theory assumes that there is no interchange of momentum between the two fluids is to some extent due to a misinterpretation. Deviations from the ground state configuration are described in terms of excitations, and most interactions within the assembly can therefore be expressed in terms of the properties of these excitations, such as their mean free path and changes in their number. On this picture, the superfluid just represents the background through which the excitations forming the normal fluid move.

4.6. THE THEORIES OF GORTER,* USUI, AND OTHERS

Gorter (1949) and Usui (1951a) have attempted to show that the formula for c_2 is not $c_2^2 = TS^2\rho_s/C\rho_n$ but is of the form (e.g. Usui)

$$c_2^2 = x(1-x) \left(\frac{\partial S}{\partial x} \right)_{p,T} \left(\frac{\partial T}{\partial x} \right)_p, \quad . \quad . \quad . \quad (114)$$

where x is said to be 'the concentration of the normal component'. I have discussed Gorter's derivation in a recent paper (Dingle 1951), and shown that it is probably valid only for the case of non-interacting material particles, i.e. for an ideal gas. Usui divides the processes leading to entropy transfer into two classes, reversible and irreversible, and assumes that irreversible transfer leads only to corrections in the higher powers of $(v_n - v_s)$; unfortunately, the particular division into reversible and irreversible transfer he has made seems to me to be somewhat arbitrary.

* I comment only briefly on the work of Professor Gorter, since he has stated his point of view clearly in a number of readily available papers and reviews; these are detailed at the end of this article.

In addition, he has assumed that the effective mass of the normal fluid is proportional to its concentration, and in his derivation of c_2 he has put $\partial \rho_n / \partial t + \text{div} (\rho_n v_n) = \Gamma = 0$, corresponding to the conservation of normal fluid, assumptions which are usually valid only for a perfect gas of material particles (Dingle 1951).

De Groot, Jansen, and Mazur (1950), consider He II as a mixture of two *components*, and write an equation of conservation of mass for each separate component (eqn. (7) of their paper), which is equivalent to taking $\Gamma = 0$. As noted above, this assumption cannot be taken over into the general theory of He II.

Kronig and Thellung (1950) attempt to show that the equations of Gorter (1949) are identical with some equations I had formulated independently (Dingle 1949). This conclusion conflicts with that of Prigogine and Mazur (1951), noted below, that further assumptions are necessary to obtain Gorter's equations from equations similar to mine. In my view there is a gap in Kronig and Thellung's argument, and they have in fact tacitly assumed that no transitions occur between the normal and superfluids when the total entropy in a volume changes due to convection processes.

Prigogine and Mazur (1951), in their interesting paper on possible formulations of hydrodynamics, arrive at equations (3.42 and 3.43 of their paper) similar* to those I had given in a previous paper (Dingle 1949 (eqn. 27)). Before applying their equations to the problem of He II, however, these authors make (§ 4 of their paper) further assumptions, such as that partial pressures do not depend explicitly on temperature, which ensure that their subsequent theory is strictly valid only for a perfect gas. Their hydrodynamical equations then reduce to those of Gorter.

4.7. FURTHER REFERENCES ON THE PROPAGATION OF SECOND SOUND IN He II.

For simplified derivations of the formula for the velocity of propagation, see Gogate and Pathak (1947), Peshkov (1948 a), and Dingle (1948). For more detailed discussions, see Tisza (1947 : see also 1938, 1940), Landau (1941), Dingle (1948, 1950), Gorter (1949), Kronig and Thellung (1950), Nakajima, Tomita and Usui (1950), Nakajima and Shimizu (1950 a ; see also 1950 b, 1951), Usui (1951 a ; see also 1951 b), but of these only the work of Landau, Dingle, and Kronig and Thellung seems to be free from the serious inadequacies commented upon in § 4.6 and particularly in Dingle (1951). For references to experimental work, see § 1.5.

For discussion of the propagation, reflection and absorption of second sound, see Peshkov (1948 a), Dingle (1948, 1950), Pellam (1948, 1949 b), Pellam and Scott (1949) and Kronig and Thellung (1950). For the application of the concept of impedance, see Osborne (1948), Dingle (1948, 1950) and Pellam and Scott (1949).

* Prigogine and Mazur's equations include two additional possible mechanisms of an irreversible nature.

On the theoretical effect of impurities (especially ^3He) on the velocity of second sound, see Landau and Pomeranchuk (1948), Pomeranchuk (1949), Khalatnikov (1951 a) and Dingle (1951, § 8). For experimental work, see Lynton and Fairbank (1950).

4.8. ON THE POSSIBILITY OF SECOND SOUND IN MEDIA OTHER THAN $^4\text{He II}$.

The fact that the existence of second sound in $^4\text{He II}$ has been experimentally demonstrated both at very low temperatures ($<0.3^\circ\text{K}$) where the only excitations seem to be phonons, and at higher temperatures where they seem to be of an entirely different nature, perhaps lends support to the theoretical conclusion that the possibility of second sound propagation should not be confined to the particular case of $^4\text{He II}$. The theoretical conditions which would have to be satisfied are:

1. ρ_n/ρ must be less than unity.
2. The coefficient of thermal expansion must be small, as otherwise first and second sounds could not be excited separately.
3. The mean free path of the excitations must be less than the wavelength (velocity divided by frequency) of second sound it is proposed to excite. (Also noted by London 1951, and Ward and Wilks 1952.)
4. Collisions between excitations must satisfy the laws of conservation of energy and momentum (cf. Ward and Wilks 1951, 1952) and not lead to any fundamental change in the energy spectrum.
5. Irreversible processes such as viscosity, thermal conduction and relaxation, must not lead to a severe attenuation.

The last three of these conditions are interconnected.

Peshkov (1947) and Ward and Wilks (1951), have suggested that second sound might be propagated in a crystal. F. London (1951) has noted that 'second light' probably could not exist, because condition (3) could not be satisfied; (neither, for that matter, could condition (1)).

4.9. ON A POSSIBLE RELATION BETWEEN SECOND SOUND AND SPECIFIC HEAT

The problem as to whether excitations of second sound waves can be considered in some sense to contribute towards the entropy and specific heat (Dingle 1949 b, c) is a difficult one, and will remain so until a satisfactory discussion of second sound is given which is based directly on *mechanical* concepts,* such as interatomic interactions, rather than on *thermal* concepts, such as fluctuations in entropy. If the suggestion is valid, it does lead at once to plausible qualitative explanations of the following two salient experimental facts in particular:

1. The high specific heat of He II, in which second sound *can* be propagated, as compared with the normal specific heat of He I, in which it cannot.

* Preliminary attempts are described in Dingle (1949 e) and Band (1949 c).

2. The fact that the velocity of second sound seems to vanish at the same temperature as that of the lambda-point in the specific heat curve. The vanishing of c_2 is due to the vanishing of ρ_s , an effective mass which can appear only when one is concerned with actual relative motion of normal and superfluid. It is therefore difficult to see why the temperature at which this occurs should be equal to T_λ , unless the specific heat is itself related in some sense to actual relative motion of normal and superfluid—i.e. to supersonic waves of second sound.

On the other hand, the description of second sound as contributing towards the specific heat cannot provide more than a formal mathematical scheme, since the apparent energy levels obtained are functions of temperature, and it is known (Rushbrooke 1940) that this is due to some averaging process performed on the real energy levels. Thus a theory of contributions from second sound could not replace the more fundamental investigations outlined in § 3. [As an illustration of the two ways in which it is possible to describe the specific heat, it is interesting to note that instead of calculating the specific heat of an ordinary perfect gas by the obvious fundamental method—calculating the kinetic energy of individual atoms—it could be derived from a modified Debye theory in which the temperature-dependence of the energy levels $E=pc$ (where $c \propto \sqrt{T}$) is explicitly taken into account.]

The paramount difficulty in formulating the required mathematical scheme is that of determining the lower wavelength limit of the supersonic waves of second sound. According to the ideas expressed in § 4.12, this must be of the order of l , the mean free path of the excitations. Since $1/l$ must increase with the number of excitations per unit volume, perhaps proportionally to their actual number N_n or to their effective mass-density ρ_n , l must become very large (as compared to the interparticle spacing) at very low temperatures, and the contribution of second sound phonons to the specific heat must then be negligible, so that only ordinary first sound phonons need be considered. Thus Landau's relation $c_2 \rightarrow c/\sqrt{3}$ remains valid.

Since the existence of a finite rather than infinite value of l is related to the degree of anharmonicity of the oscillators, it appears that the formal contribution of 'second sound phonons' may be equivalent to some correction to the Debye theory necessary to take account of anharmonic terms.

§ 5. HYDRODYNAMICS OF He II FOR LARGE VELOCITIES

The theory of the hydrodynamical equations for large velocities has not yet reached finality, even when all irreversible processes are excluded, as they will be throughout this section. Indeed, so far as the author is aware, as yet no two investigators have published an identical set of equations. The final equations of motion derived here are identical with those of Landau (1941) up to, and including, terms in the square

of the relative velocity v , a degree of accuracy to which Landau explicitly limits his calculations.

Expanding (78) in rising powers of v , and integrating over the angles, it is found that

$$\rho_n = -\frac{8\pi}{h^3} \sum_n \frac{nv^{2n-2}}{(2n+1)!} \int_0^\infty p^{2n+2} dp \left(\frac{\partial}{\partial E} \right)^{2n-1} \frac{1}{\xi \exp(E/kT) \mp 1} \quad (115)$$

The free energy \mathcal{F} , related to the Helmholtz free energy by the equation $\mathcal{F} = F + NkT \ln \xi$, is given by

$$\begin{aligned} \rho \mathcal{F} &= \pm \frac{kT}{h^3} \iiint \ln [1 \mp \xi^{-1} \exp \{(pv \cos \theta - E)/kT\}] p^2 \sin \theta dp d\theta d\phi \\ &= \rho \mathcal{F}_0 + \frac{4\pi}{h^3} \sum_n \frac{v^{2n}}{(2n+1)!} \int_0^\infty p^{2n+2} dp \left(\frac{\partial}{\partial E} \right)^{2n-1} \frac{1}{\xi \exp(E/kT) \mp 1} \\ &= \rho \mathcal{F}_0 - \frac{1}{2} \int_{v=0}^v \rho_n d(v^2), \quad (116) \end{aligned}$$

where \mathcal{F}_0 is the usual value when there is no relative motion, i.e.

$$\mathcal{F}_0 = \pm \frac{4\pi kT}{\rho h^3} \int_0^\infty \ln [1 \mp \xi^{-1} \exp(-E/kT)] p^2 dp. \quad (117)$$

The total Gibbs free energy per unit mass of the whole assembly $\Phi = F + P/\rho$, where P is the external pressure imposed on the complete assembly, is likewise decreased by the same function of v^2 .

[The free energy according to a stationary observer is seen from (116) to be a *decreasing* function of v^2 . This result is not in conflict with the expected principle of minimum free energy for the equilibrium state $v=0$, because such a principle is valid only in a coordinate system in which the assembly has no net flow. To pass to such a coordinate system, a term

$$\Sigma p \cdot v = (\rho_n v) \cdot v = \rho_n v^2 \quad (118)$$

must be added to the right-hand side of (116). Now

$$\rho_n v^2 - \frac{1}{2} \int_{v=0}^{v=v} \rho_n d(v^2) = \int_{v=0}^{v=v} v d(\rho_n v) = \int_{v=0}^{v=v} \frac{d(\rho_n v)}{dt} v \cdot dt, \quad (119)$$

is always a monotonically *increasing* function of v^2 , precisely equal, one is gratified to observe, to the work which must be done on the assembly in order to increase the relative drift velocity of the excitations from 0 to v .]

The entropy S , internal energy U , specific heat C , the number of excitations N_n , and their partial pressure P_n , may be deduced from \mathcal{F} by means of the relations

$$S = -\frac{\partial \mathcal{F}}{\partial T}, \quad U = -T^2 \frac{\partial(\mathcal{F}/T)}{\partial T}, \quad C = T \frac{\partial S}{\partial T}, \quad kTN_n = \xi \frac{\partial \mathcal{F}}{\partial \xi}, \quad P_n = -\frac{\partial \mathcal{F}}{\partial(1/\rho)}, \quad (120)$$

so that all these quantities are functions of v^2 .

It is also necessary to calculate the actual flux of free energy, $\mathcal{F}'v$ say. Since an excitation* moves in the direction of its momentum p with a (group) velocity given by Hamilton's equation as $\partial \mathcal{H}/\partial p = \partial E(p)/\partial p$,† the flux of free energy is given by

$$\mathcal{F}'v = \pm \frac{kT}{\rho h^3} \int \ln \left\{ 1 \pm \xi^{-1} \exp \left(\frac{pv - E}{kT} \right) \right\} \frac{\partial E}{\partial p} \cos \theta p^2 \sin \theta dp d\theta d\phi, \quad (121)$$

whence it may be shown that $\mathcal{F}' = \mathcal{F}$, the whole of the free energy therefore moving with the drift velocity v . Similar relations hold for the entropy, the internal energy, and the excitations themselves.

5.1. EQUATIONS OF MOTION

By Newton's second law of motion

$$\frac{dj}{dt} + \text{grad } P = 0, \quad (122)$$

where P is the pressure, and d/dt represents the total derivative with respect to time. In terms of partial derivatives, (122) leads to the usual equation

$$\frac{\partial j^i}{\partial t} + \frac{\partial \Pi^{ik}}{\partial x^k} = 0, \quad (123)$$

where now

$$\Pi^{ik} = P\delta^{ik} + \rho_n v_n^i v_n^k + \rho_s v_s^i v_s^k \quad (124)$$

is the pressure tensor. These equations were introduced into the hydrodynamics of He II by Landau (1941).

In thermodynamical theory, it is known that if the total size of a one-component assembly is made an additional variable, the differential of the internal energy must be written (e.g. Landau and Lifshitz 1938, p. 124-5):

$$dU = \Phi dM + T dS - P dV, \quad (125)$$

where Φ is the Gibbs free energy per unit mass of the total assembly and dM the differential increase in the mass of the assembly.‡ It must be remembered that U , Φ , and S , are, in general, functions of $v^2 = (v_n - v_s)^2$.

Let us suppose that all the new particles introduced into the assembly go into the ground state, so that $dS = 0$, and that the volume of the assembly is held constant, so that $dV = 0$. Then $dU = \Phi dM$. Thus the potential energy of unit mass of the 'superfluid' is simply $\Phi = \Phi(v^2)$. The equation of motion of the superfluid is therefore

$$\frac{dv_s}{dt} = -\text{grad } \Phi = -\text{grad} \left\{ \Phi_{v=0} - \frac{1}{2\rho} \int_{r=0}^{v=v_n-v_s} \rho_n d(v^2) \right\}. \quad . . . (126)$$

* Assumed capable of only translational motion (cf. § 4.21).

† *a liter.* Group velocity $= \partial v / \partial (1/\lambda) = \partial(hv) / \partial(h/\lambda) = \partial E(p) / \partial p$ by the Planck-Bohr and de Broglie relations; cf. Mott and Jones 1936, p. 92.

‡ ΦdM is usually written as μdN , where μ is the Gibbs free energy per particle (i.e. the chemical potential), and dN the differential increase in the number of particles within the assembly.

Since, according to a stationary observer, excitations are associated only with v_n , and only the excitations can have a mean free path—i.e. contribute to the viscosity—there is no viscosity term associated with v_s (see also § 6.1). Thus $\text{curl } v_s = 0$, and

$$\frac{dv_s}{dt} = \frac{\partial v_s}{\partial t} + v_s \cdot \text{grad } v_s. \quad (127)$$

5.2. HYDROSTATIC LIMIT ; THE FOUNTAIN EFFECT

When the conditions are such that only the superfluid is capable of movement, as in the fountain effect (§ 1.4), (126) shows that $\text{grad } \Phi_{v=0} = 0$ when a steady state has been attained. Since $d\Phi = dP/\rho - S dT$,

$$\frac{dP}{dT} = \rho S_{v=0}, \quad (128)$$

a relation first derived by H. London (1938, 1939). For later theoretical work, see Landau (1941), de Groot (1947, 1950), de Groot, Jansen and Mazur (1950), Ward and Wilks (1952; phonon model only). The formula agrees with observation within experimental error (for references see § 1.4).

5.3. SECOND-ORDER EQUATIONS OF TEMPERLEY AND ZILSEL

The equations of motion deduced above are identical with Landau's (1941) as far as, and including, terms in v^2 . (Landau explicitly limits his considerations to the approximation in which ρ_n is independent of v .)

Temperley (1951 b) has published a different set of equations, but he supposes that all thermodynamical quantities are independent of $v = v_n - v_s$, a procedure which seems to be inconsistent with the method of calculating ρ_n in terms of the energy spectrum of the excitations.

Zilsel (1950), in an ingenious application of Eckart's (1938) variational principle, also assumes that S , U , and ρ_n are independent of v , and as pointed out by Temperley (1951 b), appears to arrive at a contradiction in that he finds $\partial U / \partial (\rho_n / \rho) = \frac{1}{2} v^2$. This is hardly surprising, since we have seen that in reality the thermodynamical quantities are all functions of v^2 . In any case, in the second and higher orders of the theory, U , S , and ρ_n cannot be treated as separate variables in the variational process, as in fact Zilsel has treated them, since we have seen that they are linked by (116).

Both Temperley and Zilsel write their equations of motion in terms of a quantity $S_n = \rho S / \rho_n$, the 'specific entropy of the normal fluid'. This does not seem to me to be a convenient parameter when S_n can vary, as it does if the velocities are high, since S_n (unlike S) has no physical significance, and is not susceptible to ordinary thermodynamic transformation. Zilsel implies that the term $(v_n - v_s) d \ln S_n / dt$ which appears in his equation for dv_n / dt is *additional* to those obtained on Landau's theory, but I maintain that on the contrary it may be deduced from Landau's equations if one puts $\rho S = \rho_n S_n$ and calculates dv_n / dt . Temperley obtains terms involving S_n in his expressions for both dv_n / dt and dv_s / dt .

The apparent defects in these theories may be traced to the lack of a sufficiently fundamental approach, values of the effective mass and the thermodynamical quantities being postulated instead of being deduced from the energy spectrum as modified by the drift motion.

5.4. SECOND SOUND OF LARGE AMPLITUDE ; SHOCK WAVES

Solving Landau's equations to the next higher approximation than that equivalent to § 4.2, Khalatnikov (1951 b) found that

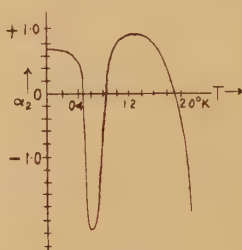
$$c_2 = c_{20} + \alpha_2 v_n, \quad \dots \dots \dots (129)$$

where

$$c_{20}^2 = \frac{TS^2\rho_s}{C\rho_n}; \quad \alpha_2 = \frac{TS}{C} \frac{\partial}{\partial T} \ln \left(\frac{Cc_{20}^3}{T} \right). \quad \dots \dots \dots (130)$$

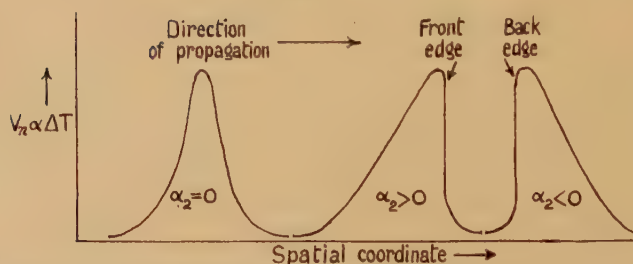
Here α_2 is a dimensionless quantity which is positive for $0 < T < 0.5^\circ \text{ K}$ and $0.9^\circ < T < 1.9^\circ \text{ K}$, but negative for $0.5^\circ < T < 0.9^\circ \text{ K}$ and $1.9^\circ < T < 2.186^\circ \text{ K}$ (fig. 5).

Fig. 5



α_2 as a function of temperature.

Fig. 6



Distortion of a second-sound pulse of large amplitude. The pulses are travelling towards the right.

When α_2 is positive, (129) shows that the front edge of a positive temperature pulse (corresponding to positive v_n) should become sharper, and the back edge blunter (fig. 6). Now if v_n can be made sufficiently large for the propagation velocity c_2 to become a non-unique function of position, a discontinuity in temperature is propagated through the liquid. Thus if α_2 is positive, a 'front edge' shock wave can be formed. On the other

hand, when α_2 is negative, the back edge should sharpen, and the front edge blunten, so that 'back-edge' shocks might be formed. [Back-edge shocks are unknown for ordinary sound, since the corresponding α is always positive.]

If, following Khalatnikov, we assume a theorem of ordinary first sound shock-front theory to the effect that (e.g. Courant and Friedrichs 1948, p. 159) *the velocity of a forward-facing shock front is in first order just the mean value of the velocities of the forward-facing sound waves ahead and behind the shock-front*, the velocity of a temperature shock must be

$$(c_2)_{\text{shock}} = c_{20} + \frac{1}{2}\alpha_2(v_{n1} + v_{n2}), \quad . \quad . \quad . \quad (131)$$

where v_{n1} and v_{n2} are the velocities of the normal fluid on either side of the shock. The theory is in satisfactory agreement with the experiments of Osborne (1951).

An earlier treatment is due to Temperley (1951 b). He gives an interesting discussion of the whole problem, but the equations of motion he has used seem to be open to question (§ 5.3). See also Reines (1951).

5.5. CRITICAL VELOCITIES

It is clear from (115) that ρ_n increases monotonically with v^2 , so that the superfluid density $\rho_s = \rho - \rho_n$ decreases as the relative velocity is increased. The effect of increasing v is therefore similar to that of increasing T , the superfluid density decreasing until finally all superfluidity vanishes. The critical velocity at which this finally occurs decreases markedly as the lambda-point is approached, since it depends on the value of $[\rho_s(T)]_{v=0}$. Thus there is a critical $v(T)$ curve for superfluid helium analogous to the critical $H(T)$ curve for superconductors.

For phonons it may be deduced from (115) that $(\rho_n/\rho)_{\text{phon}}$ is increased by a factor $(1 - v^2/c^2)^{-3}$ over that for $v \rightarrow 0$, leading to a critical velocity in an assembly in which phonons are the only excitations, of magnitude

$$v_{\text{crit}} = c \left\{ 1 - \left(\frac{4U_0}{3c^2} \right)^{1/3} \right\}^{1/2}, \quad . \quad . \quad . \quad (132)$$

where $U_0(T)$ is the internal energy per unit mass in the static system ($v=0$). Thus at very low temperatures, $v_{\text{crit}} \sim c = 237$ m/s.

For rotons, assuming the energy spectrum $E = \Delta + p^2/2\mu$, the sole effect of high velocities is to change the exponential factor in $(\rho_n/\rho)_{\text{rot}}$ to $\exp \{(\frac{1}{2}\mu v^2 - \Delta)/kT\}$. The critical velocity is thus of the order of $(2\Delta/\mu)^{1/2} \sim 60$ m/s, the precise magnitude depending on the temperature. On the other hand, if we assume that $E = \Delta + (p - p_0)^2/2\mu$, $(\rho_n/\rho)_{\text{rot}}$ is increased by a factor of about $* 3z^{-2} (\cosh z - z^{-1} \cdot \sinh z)$ where $z = p_0 v/kT$; the critical velocity is then of the order of $\Delta/p_0 \sim 70$ m/s.

In a condensed Bose-Einstein system, if we take $E(p)$ equal to $Ap^{1/r}$ as in § 3.22, we find that

$$v_{\text{crit}} \sim Ar(kT)^{1-r} \sim c_2 \sim 20 \text{ metres/sec.}$$

* Assumes that $p_0 \gg (2\mu\Delta)^{1/2}$.

The alternative self-consistent field (§ 3.222) leads to the result that

$$v_{\text{crit}} \sim (2\Delta/\mu)^{1/2} \sim 60 \text{ metres/sec,}$$

as for rotons.

Although these arguments give qualitatively the observed behaviour in so far as $v_{\text{crit}} \rightarrow 0$ as $T \rightarrow T_\lambda$, the experimentally measured critical velocities are far smaller—of the order of a few *cm/sec* (e.g. Atkins 1951, and review in this issue; Hollis-Hallett 1950, 1952)—and it must be supposed that some other process is responsible (see § 6.5). All the same, it should be borne in mind that the mechanism described always exists, and possibly predominates in the immediate neighbourhood of the lambda-point. We return to the problem of critical velocities in § 6.5.

The values given above for the critical velocities in phonon and roton assemblies virtually agree with those of Landau (1941). He assumes that no new excitations will be produced unless such a process would be energetically favourable. The condition that no new excitations appear is then (see also Ginsburg 1950)

$$p \cdot v < E(p); \quad \text{i.e. } v_{\text{crit}} = \{E(p)/p\}_{\text{minimum}}. \quad (133)$$

For phonons, $E(p) = pc$, whence $v_{\text{crit}} = c$. For rotons

$$\mu v_{\text{crit}} = (2\mu\Delta + p_0^2)^{1/2} - p_0.$$

It seems to the author, however, that this mode of derivation ignores the 'tunnel' effect.

5.6. CRITICAL VELOCITIES IN FINE CAPILLARIES AND FILMS

Ginsburg (1950) has suggested a theory of the critical velocities for flow in fine capillaries and films. His theory is similar to that of the critical velocity in the bulk liquid (§ 5.5). In a fine channel, it can no longer be assumed that the momentum p is isotropic. If p_{\parallel} is the momentum in the direction of transfer, and p_{\perp} that perpendicular to it, the appropriate generalization of (133) is

$$v_{\text{crit}} = \{E(|p|)/p_{\parallel}\}_{\text{minimum}}. \quad (134)$$

For rotons (assuming $p_0 = 0$), $E(|p|) = (p_{\parallel}^2 + p_{\perp}^2)/2\mu$, and $p_{\perp}^2 \sim \pi^2 \hbar^2/d^2$, where d is the width of the channel. Minimizing E/p_{\parallel} with respect to d , it is found that

$$v_{\text{crit}} \sim \pi \hbar / \mu d. \quad (135)$$

For the He film, or for capillaries sufficiently narrow for only superfluid to be able to move within, (135) gives a critical velocity of the observed order of magnitude of a few centimetres per second.

Mott (1949) has suggested a theory based on the property (cf. Bijl, de Boer and Michels (1941)) that in a Bose-Einstein assembly composed of atoms in the same state, the change in potential energy if one atom is made to go into a different state is equal to the interaction energy per particle. This assumes that (1) only binary collisions need be considered, and (2) the energy integral is positive, i.e. that no molecular helium can be formed.

It is thus very difficult for moving He II to slow down, since any attempt to stop the moving (superfluid) atoms one by one would increase the potential energy, while any attempt to stop them all at once would require too great a change in momentum.

In the case of a fine capillary of diameter d , suppose that a central core of stationary fluid of diameter d_{stat} has been formed. Then if l is the mean interatomic distance, the number of moving atoms is $\pi(d^2 - d_{\text{stat}}^2)/4l^3$ per unit length of capillary, and the number of atoms forming the boundary between stationary and moving parts, i.e. the number of atoms which are nearest neighbours to atoms in different states, is $\pi d_{\text{stat}}/l^2$ per unit length of capillary.

By dimensional considerations, the interaction energy per particle is about \hbar^2/ml^2 . Thus, per unit length of capillary,

$$\left. \begin{aligned} \text{kinetic energy} &= \frac{1}{2}mv^2 \frac{\pi(d^2 - d_{\text{stat}}^2)}{4l^3}; \\ \text{potential energy} &= \frac{\hbar^2}{ml^2} \frac{\pi d_{\text{stat}}}{l^2}. \end{aligned} \right\} \quad \dots \quad (136)$$

Differentiating with respect to d_{stat} , it is found to be favourable for d_{stat} to increase only if $v > \hbar/m(ld_{\text{stat}})^{1/2}$. Assuming that a nucleus of stationary liquid can spread up from the bulk liquid, it can therefore only widen sufficiently to prevent further flow if $v \geq v_{\text{crit}}$, where

$$v_{\text{crit}} \sim \hbar/m(ld_{\text{min}})^{1/2}, \quad \dots \quad (137)$$

d_{min} being the width of the narrowest constriction in the capillary. A similar result may be obtained for the case of a film.

§6. EFFECTS OF IRREVERSIBLE PROCESSES ON THE HYDRODYNAMICS OF He II

6.1. VISCOSITY

In the presence of a gradient in the drift velocity of the excitations, a net transfer of momentum from point to point can occur. This momentum transfer, relative to a stationary observer, is proportional both to the mean free path of the excitations and to the gradient in the drift velocity of the excitations measured relative to the stationary observer. The viscosity η is thus to be associated with v_n , and (122) is modified to

$$\frac{dj}{dt} + \text{grad } P - \eta(\nabla^2 v_n + \frac{1}{3} \text{grad div } v_n) = 0. \quad \dots \quad (138)$$

The entropy gain due to this irreversible process is quadratic in the velocities, and may be neglected as a first approximation. Thus eqns. (84) and (126), and of course the equation of mass-conservation (82), remain approximately true.

In an extended medium, it is then found that the distance in which the amplitude of sound of frequency $\omega/2\pi$ falls to $1/e$ of its initial value is $L_1 = 3c^3\rho/2\eta\omega^2$ for first sound, and $L_2 = (\rho_n/\rho_s)(3c_2^3\rho/2\eta\omega^2)$ for second sound (e.g. Dingle 1950, Kronig and Thellung 1950).

In a narrow circular tube of radius r , the corresponding distances are $L_1 = c\rho r(2/\rho_n\eta\omega)^{1/2}$ for first sound, and $L_2 = (\rho_n/\rho_s)c_2\rho r(2/\rho_n\eta\omega)^{1/2}$ for second sound (e.g. Peshkov 1948, Dingle 1950). The steady flow of He II through thin tubes has been discussed by F. London and Zilsel (1948).

6.11. Value of the Viscosity Coefficient

Tisza (1947, see also 1938, 1940) has suggested the gas-kinetic relation $\eta \propto T^{1/2}$. (See also Eisenschitz 1951.)

Landau and Khalatnikov (1948, 1949) have attempted to calculate the mean free path of phonons and rotons, and thence the viscosity. They find that the mean free path, and hence the viscosity, should increase as the temperature is lowered, becoming very large at extremely low temperatures. Their final expressions are

$$l_{\text{phonon}}^{-1} = \begin{cases} 3.4 \times 10^6 T^{9/2} \exp(-\Delta/kT) & T > 1^\circ \text{K} \\ 1.1 \times 10^8 T^{9/2} \exp(-\Delta/kT) + 5.6 \times 10^{-2} T^9 & T < 0.8^\circ \text{K}, \end{cases} \quad (139)$$

where l_{phonon} is the mean free path of the phonons, and

$$\eta \times 10^5 = \begin{cases} 1 + 8.7 \times 10^{-4} T^{-1/2} \exp(\Delta/kT) & T > 1^\circ \text{K} \\ 7.8 \times 10^{-5} \{T^{1/2} \exp(-\Delta/kT) + 4.8 \times 10^{-6} T^5\}^{-1} & T < 0.8^\circ \text{K}. \end{cases} \quad (140)$$

On the same basis, Khalatnikov (1950) has calculated the time lag before establishment of equilibrium—i.e. the second viscosity—and shown that it could explain the increasing attenuation of first sound found below about 1.5°K (Pellam and Squire 1947, Atkins and Chase 1951).

These calculations seem to be subject to two criticisms:

1. Part of the scattering is supposed to be due to rotons, concerning which very little is known. It is by no means obvious that a hypothesis (and in particular a rather arbitrary energy spectrum) adequate for a description of the temperature variation of the specific heat is also adequate for a description of the scattering processes.

2. Landau and Khalatnikov consider only scattering processes in which momentum is conserved. In calculating the phonon-phonon scattering, this requires that at least four phonons must take part. It is possible, however, that 'Umklapp' processes, in which phonon momentum is not conserved, are important, since they involve only three phonons (Temperley, private communication).

6.2. THERMAL CONDUCTION

If K is the ordinary heat conductivity not involving movement of the normal and superfluids, the equation of entropy conservation becomes, at least approximately,

$$\frac{\partial(\rho S)}{\partial t} + \rho S \operatorname{div} v_n - \frac{K}{T} \nabla^2 T = 0. \quad (141)$$

This leads to an attenuation in an extended medium, such that (Dingle 1950) $L_1 = 2\rho Cc/Kw^2 T\alpha^2$ and $L_2 = 2\rho Cc_2^3/Kw^2$; here α is the coefficient of thermal expansion, and C the specific heat per unit mass.

In a hollow narrow tube made of material of thermal conductivity K_{sol} , specific heat per unit mass C_{sol} and density ρ_{sol} , conduction and viscous processes together lead to an attenuation such that*

$$L_2 = \rho r c_2 \left\{ \rho_s \left(\frac{\eta \omega}{2 \rho_n} \right)^{1/2} + \frac{2 c_2}{C} \left(\frac{K_{\text{sol}} \rho_{\text{sol}} C_{\text{sol}} \rho_n}{\eta} \right)^{1/2} \right\}^{-1}. \quad (142)$$

This process appears to be directly connected with Kronig and Thellung's (1950) 'third sound', an attenuated wave motion depending on the simultaneous presence of viscosity and thermal conduction.

6.3. RELAXATION PROCESSES

Meyer and Band (1947, 1948, 1949) have attempted to calculate the attenuation of second sound on the assumption that there exists a time of relaxation τ . Most irreversible processes, however, are due to *some* time of relaxation, and I have not always been able to gather precisely to what ultimate process or processes Meyer and Band refer. In my view, a single calculation of the attenuation independent of the basic mechanism is hardly sufficient. Specific relaxation processes have been proposed by Dingle (1951) and Gorter, Taconis and Beenakker (1951). See also Kronig, Thellung and Woldringh (1952).

[Meyer and Band assert (1949) that 'second sound is thermodynamically possible only in the absence of thermal equilibrium between superfluid and normal components of He II, since otherwise heat would have to flow up a temperature gradient in one-half of the period, in contradiction to the second law of thermodynamics'. Surely, however, the law that heat cannot flow up a temperature gradient is confined to cyclical processes in assemblies on which no external work is being done, and cannot therefore be applied to half wave-lengths. The second law is actually introduced explicitly into the theory in the form of the equation of entropy conservation.]

6.4. MUTUAL FRICTION

It is an experimental fact that although the heat flow and the fountain effect are each *non-linear* functions of the temperature gradient, they are nevertheless proportional to each other (Allen and Reekie 1939, Duyckaerts 1943, Keesom and Duyckaerts 1947, Mellink 1947). Gorter (1948) and Gorter and Mellink (1949) have given the ingenious explanation that there exists a mutual force between the normal and superfluids, equal in magnitude for each fluid, but of opposite sign. The postulated force is found to be roughly proportional to the cube of the relative velocity, i.e. to v^3 .

Zilsel (1950) has suggested that this force arises theoretically from terms in the equations of motion representing the possibility of transitions between normal and superfluids, taken together with the creation of entropy due to some irreversible process, such as viscosity. Since the force must change sign with v , it must be of the form $vf(|v|)$. It is

* The right-hand side of eqn. (12.7) of Dingle (1950) should be multiplied by a factor 2.

tempting to put $f(|v|) \propto v^2 + O(v^4)$, thereby providing a theoretical explanation of the cube law found experimentally* (see, for instance, Prigogine and Mazur 1951, eqn. (3.35)). In my opinion, however, this argument is not altogether conclusive, since theoretical expressions are known which involve some power of the *modulus* of a vector rather than the square of the vector.† This possibility is usually removed by the necessity of continuity in some of the derivatives of the vector at its vanishing point, but I do not see any obvious reason for such a condition on the derivatives of the frictional force.

It is as yet an open question whether the theoretical frictional force should act equally (but in opposite sense) on the normal and superfluids. There seems to be no *a priori* reason why it should.

6.5. CRITICAL VELOCITIES

The Gorter-Mellink frictional term itself leads, of course, to a sort of very blurred critical velocity. It is also possible that irreversible processes lead to a marked increase in the velocity-dependence of $\rho_n = \rho_n(v^2)$, and hence by the mechanism of § 5.5 to a *sharp* critical velocity smaller than that calculated on the assumption that irreversible processes are absent.

6.6. COMMENTS ON IRREVERSIBLE PROCESSES

It will be appreciated that a really satisfactory theory of irreversible effects in He II necessitates a more fundamental approach. The beginnings of such a theory may be detected in recent work on the application of the thermodynamics of irreversible processes (e.g. Prigogine and Mazur 1951), and in the work of Landau and Khalatnikov (1949, 1950) on collisions of phonons and rotons.

§ 7. HELIUM FILMS

The helium film (§ 1.7; review by Jackson in this issue) is assumed to be similar in composition to the bulk liquid at the same temperature, and to be sufficiently thin for the normal fluid to cling to the surface, as in the Andronikashvili experiment, so that only the superfluid partakes in the flow. The transfer rate is supposed to be limited by some critical velocity (§ 5.6). It then remains to explain why such a thick film (about 100 atoms thick) can form on a surface partly immersed in He II, but not on a surface partly immersed in He I.

Frenkel (1940) and Schiff (1941) have given theories according to which the helium film is essentially due to the ordinary van der Waals forces between the helium atoms and the surface of the wall, and also, of course, between the different helium atoms themselves. The potential energy of attraction between two atoms is proportional to the inverse sixth power of their separation. At a distance x from the wall, the

* But see review by Atkins in this issue.

† For instance, the amplitude of the de Haas-van Alphen effect (see e.g. Shoenberg 1939) is proportional to

$$|H|^{-3/2} \sin(2\pi E_0/\beta |H| - \frac{1}{4}\pi) / \sinh(2\pi^2 kT/\beta |H|).$$

potential energy of a single atom will therefore be proportional to x^3 , since one must integrate up all the individual energies involved. Minimizing the sum of the van der Waals and gravitational energies, it is found that the thickness d at a height H above the free surface of the bulk liquid is proportional to $H^{-1/3}$. It is supposed that He I cannot form such a film either because its viscosity creates such a time delay that flow from the bulk liquid cannot replenish loss by evaporation from the film, or because the surface energies involved are favourable only for He II.

Bijl, de Boer, and Michels (1941) have put forward an interesting theory in which zero-point energy is considered to be the dominant factor. Suppose for the sake of argument that a film has already been formed: then if an attempt is made to thicken it, its gravitational energy is increased, but the total zero-point energy is decreased, for each particle will now have more space in which to move, an effect outweighing the fact that more particles will be present. The equilibrium thickness is such that these energy changes exactly balance, so that the total energy is at a minimum.

These authors assume that the appropriate wave-function is that of a free particle in its lowest state. The Schrödinger equation is

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2m}{h^2}E\psi = 0, \quad (143)$$

for which the solution with lowest energy is

$$\psi \propto \sin(\pi x/d); \quad E = h^2/8md^2 \text{ per atom.} \quad (144)$$

The number of atoms in the film is proportional to its thickness d , so that

$$d(mgh) + d(h^2/8md^2), \quad (145)$$

must be minimized with respect to the parameter d . This yields the result

$$d = h/m(8gH)^{1/2} \propto H^{-1/2}. \quad (146)$$

This theory must be criticized on the following grounds:

1. It is difficult to believe (Mott 1949) that the density of the film has a maximum at the centre and falls off to zero at the sides, as would be implied by a probability distribution of the form

$$|\psi|^2 \propto \sin^2(\pi x/d). \quad (147)$$

In the bulk liquid it is clear that the atoms in the ground state could not possess this type of wave-function, since for temperatures below the lambda-point a finite fraction of the atoms are in the lowest state, and, if (147) were true, they would all congregate together near the centre of the vessel, an effect which would be easily observed—for instance by the increase in refractive index near the centre. It is still just conceivable, however, that this wave-function is a reasonable approximation for thin films, but fails for assemblies of larger dimensions.

2. It is not easy, on this theory, to see how the film is first formed, since the total energy of the film (145) tends to infinity if $d \rightarrow 0$. This is not really a serious difficulty, since it is plausible to suppose that some

sort of film would start to form due to surface tension effects brought about by the attractive van der Waals forces, and then would grow in order to reduce the zero-point energy.

Temperley (1949 a) has proposed an explanation incorporating the ideas of both the preceding theories. Considering first only the interactions between an atom and the wall, its wave-function is

$$\frac{d^2\psi}{dx^2} + \left(\frac{8\pi^2m}{h^2} E + \frac{k^2}{(p+x)^3} \right) \psi = 0, \quad \dots \quad (148)$$

the term in $(p+x)^{-3}$ representing the van der Waals energy between the atom and the wall. The quantity p is the distance of closest approach to the wall, equal to the atomic diameter a if the wall is bare, or to $(a+d)$ if there is a film of thickness d . If the appropriate boundary conditions for ψ are inserted, E will automatically include both the zero-point energy and the energy of attraction. For $E=0$, $\psi \propto (p+x)^{1/2} J_1\{2k(p+x)^{-1/2}\}$, for which the first non-trivial zero is given by $p+x = (2k/3.83)^2 \sim 3 \times 10^{-7}$ cm for a glass wall. This is the maximum possible thickness of a film which relies only on forces between individual atoms and the wall.

If the mutual interaction between the atoms forming the film is regarded as a self-consistent field in which a given atom must move, the wave-equation for such an atom reads

$$\frac{d^2\psi}{dx^2} + \left\{ \frac{8\pi^2mE}{h^2} + \frac{k^2}{(a+d+x)^3} + \frac{l^2}{(a+x)^3} - \frac{l^2}{(a+d+x)^3} \right\} \psi = 0. \quad (149)$$

Here the last two terms arise from the interatomic van der Waals forces within the film, and the term involving k^2 represents the van der Waals energy between the atom and the wall. An approximate value of E may be deduced by means of the variational principle. Balancing this energy against the gravitational energy yields a relation for the rate of change of thickness with height which agrees in order of magnitude with experiment (see review by Jackson in this issue).

On this theory, the variation of film thickness with temperature (see review by Jackson) is explained as being due to the existence of a small number of low-energy 'bound' states representing an adsorbed atom at the surface of the film. Because of their low statistical weight, these states would only fill above the lambda-point if there would be an appreciable energy gain, i.e. only if the film is thin.

Band (1949 b, 1951) has discussed the adsorption isotherms of helium, with special reference to temperatures above the lambda-point.

ACKNOWLEDGMENTS

I should like to thank Professor J. F. Allen, Dr. D. ter Haar, Professor N. F. Mott, Mr. J. K. Potts, Dr. D. Shoenberg, Miss E. C. Taylor and Mr. H. N. V. Temperley for helpful comments on the first draft of this article.

APPENDIX

In the partition function (44), i.e.

$$Z = \sum_s z_s^N \prod_{r \neq s} (1 - z_r/z_s)^{-1} = \sum_s \exp [N \ln z_s - \sum_{r \neq s} \ln (1 - z_r/z_s)] \quad (\text{A } 1)$$

we have

$$\ln \left(\frac{-(s+1)^{\text{th}} \text{ term}}{s^{\text{th}} \text{ term}} \right) \\ = (N+1) \ln \left(\frac{z_s}{z_{s-1}} \right) - \sum_{r \neq s-1, s} \left[\ln \left(1 - \frac{z_r}{z_s} \right) - \ln \left(1 - \frac{z_r}{z_{s-1}} \right) \right] \quad (\text{A } 2)$$

$$= (N+1) \ln \left(\frac{z_s}{z_{s-1}} \right) - (\ln z_s - \ln z_{s-1}) \frac{\partial}{\partial \ln z_{s-1}} \sum_{r \neq s-1, s} \ln \left(1 - \frac{z_r}{z_{s-1}} \right) - \dots \quad (\text{A } 3)$$

$$= - \left(\frac{E_s - E_{s-1}}{kT} \right) \left[N+1 - \sum_{r \neq s-1, s} \frac{1}{\exp (E_r - E_{s-1})/kT - 1} \right. \\ \left. - \left(\frac{E_s - E_{s-1}}{kT} \right) \sum_{r \neq s-1, s} \frac{\exp (E_r - E_{s-1})/kT}{\{\exp (E_r - E_{s-1})/kT - 1\}^2} \dots \right] \quad (\text{A } 4)$$

The assembly is in its 'condensed' state if this quantity is large and negative, for then successive terms in the partition function decrease so rapidly that only the first one need be retained, and it is this initial term which leads to the 'condensation' relations (46) and (47).

For a perfect gas $(E_s - E_{s-1})/kT \sim \hbar^2/mkTV^{2/3}$, and thus

$$\ln \left(\frac{-2\text{nd term}}{1\text{st term}} \right) \sim - \frac{\hbar^2}{mkTV^{2/3}} \left[N - \sum_{r \neq 0} \frac{1}{\exp (E_r/kT) - 1} \right] \\ \sim -N_n^{1/3} \left\{ \frac{N}{N_n} - 1 \right\} \quad (\text{A } 5)$$

where $N_n = \sum_{r \neq 0} (\exp (E_r/kT) - 1)^{-1}$. (The terms omitted from within the curly brackets in (A 5) are of order $N^{-1/3}$ at most.) It may be shown that the quantity in square brackets in (A 4) increases with s . The assembly is therefore 'condensed' if $N > N_n$, the number of particles in the ground state then being $N - N_n$ by (47), and the number in all the excited states N_n by (46). The number in the first excited state, $N_1 = (\exp (E_1/kT) - 1)^{-1}$ by (46), is approximately $kT/E_1 \sim mkTV^{2/3}/\hbar^2 \sim N_n^{2/3}$. In the limit $N \rightarrow \infty$ (but $N/N_n = \text{constant} > 1$), the first term in the series for the partition function becomes infinitely greater than the second. Thus (46) and (47) are *exact* for an infinite 'condensed' assembly.

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Wave Propagation and Flow in Liquid Helium II

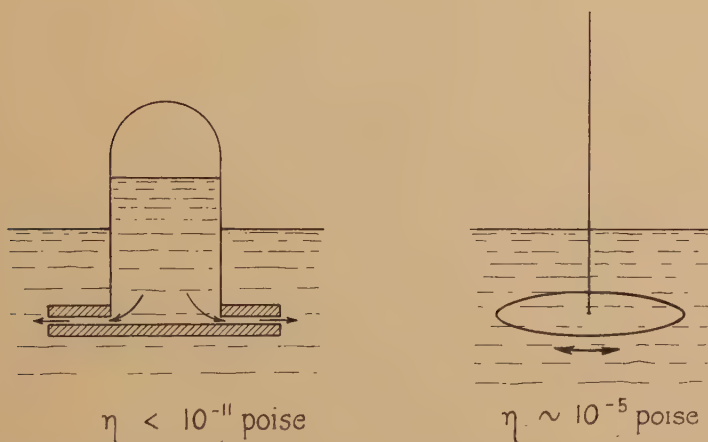
By K. R. ATKINS

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§1. INTRODUCTION

At a temperature of 2.19°K , usually referred to as its λ -point, liquid helium undergoes a transition and below this temperature exists in the modification known as liquid helium II, which has some extraordinary properties. The most unusual of these is its 'superfluidity'. It will flow with a velocity of many centimetres per second through channels only 10^{-5} cm wide. Under these conditions its apparent viscosity is certainly less than 10^{-11} poise. On the other hand, the viscosity can be measured by studying the damping of the motion of a disc performing torsional oscillations in the liquid, and the apparent value of the viscosity is then found to vary from about 2×10^{-5} poise near the λ -point to about

Fig. 1



Flow through narrow channels

Damping of an oscillating disc

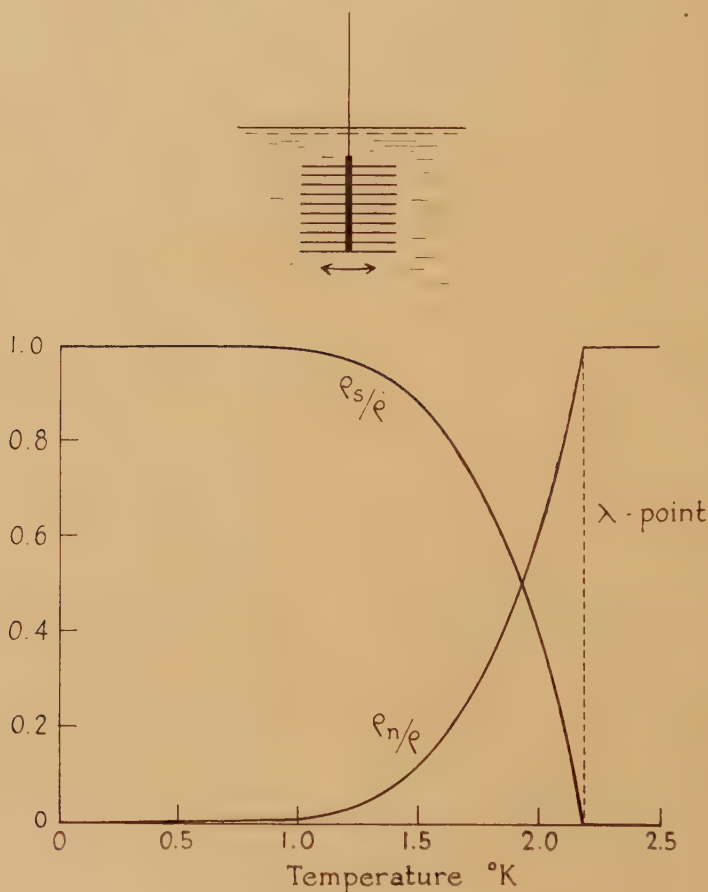
The two different methods of measuring the viscosity of liquid helium II.

10^{-6} poise at 1°K . Apart from the strong disagreement between the two methods, it seems that neither method can determine the viscosity uniquely. In the case of flow through narrow channels, the apparent viscosity is found to vary with the width of the channel and the pressure gradient. In the case of the oscillating disc, the apparent viscosity begins to increase if the peripheral velocity of the disc is made too large. It is clear that we are faced here with a novel type of hydrodynamical behaviour, to be described only in terms of an entirely new set of hydrodynamical equations.

The first step towards setting up these equations is the two fluid hypothesis associated with the names of London (1938), Tisza (1947) and Landau (1941). Liquid helium II is considered to be some sort of intimate mixture of two components, a normal component and a superfluid component, so that its total density ρ can be separated into a normal density ρ_n and a superfluid density ρ_s :

$$\rho = \rho_n + \rho_s \quad (1)$$

Fig. 2

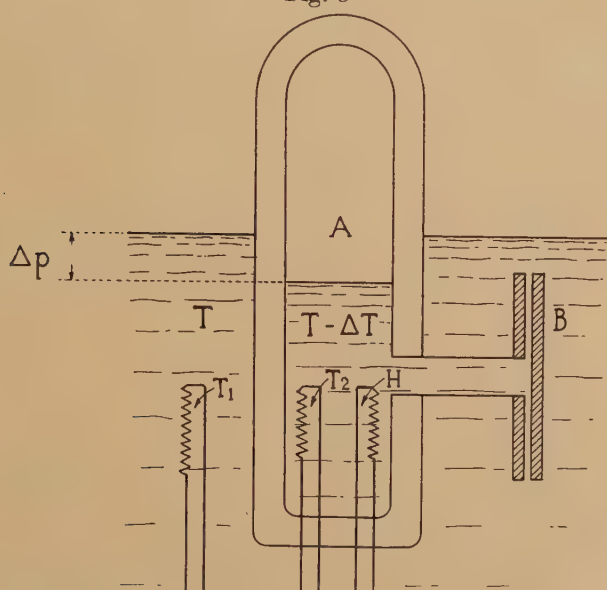


Andronikashvili's experiment.

The normal component is considered to have a normal viscosity and is therefore responsible for the damping of the motion of an oscillating disc and the relatively high value of the apparent viscosity deduced from this damping. The superfluid component, on the other hand, is the part capable of flowing through very narrow channels with high velocities, and it behaves as though it had zero viscosity. This division into two

components was demonstrated in a very convincing manner in an experiment performed by Andronikashvili (1946). A pile of discs performed torsional oscillations in the liquid (see inset to fig. 2). The gap between the discs (0.21 mm) was sufficiently small so that, above the λ -point, all the liquid between the discs was dragged round by them and contributed to the effective moment of inertia of the system. Below the λ -point, however, only the normal component moved with the discs, the superfluid component being subject to no frictional force which would have brought it into action. Therefore, as the temperature was lowered below the λ -point, the period of oscillation steadily decreased and it was possible to deduce the fraction, ρ_n/ρ , of liquid contributing to the moment of inertia of the system. The results are shown in fig. 2, from which it will be seen that the fraction, ρ_s/ρ , of superfluid increases from zero at the λ -point to unity at 0°K .

Fig. 3



Kapitza's apparatus.

In addition to its zero viscosity, the superfluid component also has zero entropy. Fig. 3 is a schematic representation of the apparatus used by Kapitza (1941) to prove this. The thermally isolated vessel *A* communicated with the helium bath through the narrow channel *B*, $\sim 10^{-4}$ cm wide, which was made by pressing together two optically polished quartz surfaces. When superfluid flow started into the inside of the vessel, the inside temperature, as recorded on the resistance thermometer T_2 , began to fall. In order to maintain the inside temperature at the same value as the bath temperature, it was necessary to supply to the heater *H* an amount of heat equal to the total heat content

of that quantity of liquid which had passed through the slit. Another way of describing this is to postulate that the moving superfluid component was effectively at the absolute zero of temperature, and upon emerging from the inner end of the channel had to be warmed up to the temperature of the bath.

The small heat content of the superfluid component results in some peculiar thermal effects. When there is a source of heat immersed in the liquid, Le Chatelier's principle tells us that the cold superfluid component will move towards this source and the warm normal component will move away from it. Because the superfluid component is effectively at the absolute zero of temperature, this type of counterflow is a very efficient convection process, explaining the observed fact that liquid helium II is a very good conductor of heat, under suitable circumstances more than 1000 times better than copper at room temperature. The ability of the superfluid component to move when subjected to a temperature gradient gives rise to a phenomenon known as the 'fountain effect' or 'thermo-mechanical effect'. In the apparatus of fig. 3, it is possible for the inner level to settle down to an equilibrium position below that of the outer level provided that the temperature inside is lower than outside. The tendency for the pressure gradient to force the liquid inwards is then exactly compensated by the tendency for the temperature gradient to force the liquid outwards. H. London (1939) has shown thermodynamically that, provided the entropy of the liquid flowing through the channel is exactly zero, the pressure Δp which can be maintained against a temperature difference ΔT should be given by

$$\frac{\Delta p}{\Delta T} = \rho S, \quad (2)$$

where S is the entropy of the bulk liquid, normal plus superfluid. This relationship was confirmed by Kapitza.

§2. FLOW PHENOMENA

(a) *The Hydrodynamical Equations*

The exact form of the hydrodynamical equations is still a controversial matter, but, for the purposes of the present discussion, it will be sufficient to write them in a form based on the original ideas of Landau and Tisza :

$$\rho_s \frac{D\mathbf{v}_s}{Dt} = -\frac{\rho_s}{\rho} \text{grad } p + \rho_s S \text{ grad } T - F_{sn}(\mathbf{v}_s - \mathbf{v}_n) - F_s(\mathbf{v}_s), \quad . . . (3)$$

$$\begin{aligned} \rho_n \frac{D\mathbf{v}_n}{Dt} = & -\frac{\rho_n}{\rho} \text{grad } p - \rho_s S \text{ grad } T + F_{sn}(\mathbf{v}_s - \mathbf{v}_n) - F_n(\mathbf{v}_n) \\ & + \eta_n (\nabla^2 \mathbf{v}_n + \frac{1}{3} \text{grad div } \mathbf{v}_n). \quad (4) \end{aligned}$$

Here \mathbf{v}_s and \mathbf{v}_n are the velocities of the superfluid and normal components respectively, and η_n is the viscosity associated with normal component. The first point to notice is that it is necessary to write two equations,

one for each of the two components. Equation (3) is the equation of motion of the superfluid component and eqn. (4) is the equation of motion of the normal component. The acceleration terms $\rho_s \frac{D\mathbf{v}_s}{Dt}$, $\rho_n \frac{D\mathbf{v}_n}{Dt}$ and the terms in grad p are similar to those normally encountered in classical hydrodynamics, but there are also terms in grad T , expressing the fact that the superfluid component will tend to move towards regions of high temperature, whereas the normal component will tend to move towards lower temperatures. A viscosity term $\eta_n(\nabla^2 \mathbf{v}_n + \frac{1}{3} \text{grad div } \mathbf{v}_n)$ appears only in the equation for the normal component. There are, however, other frictional terms F_s , F_n and F_{sn} expressing the observed fact that true superfluidity occurs only under ideal conditions, and that in many experiments there is evidence for new frictional forces producing a breakdown of the simple concepts of superfluidity and the two-fluid theory. F_{sn} represents a mutual friction between the two components of the type first postulated by Gorter and Mellink (1949). It therefore depends only on the relative velocity $\mathbf{v}_s - \mathbf{v}_n$ and is equal and opposite in the two equations. F_s and F_n are possible forces inherent in the two components separately, independently of the behaviour of the other component. F_{sn} , F_s and F_n may contain operators such as grad, div and curl.

Although these two hydrodynamical equations will provide a very convenient basis for discussion, it is important to realize their limitations. They must, of course, be supplemented by two more equations such as :

$$\frac{\partial \rho}{\partial t} + \text{div} (\rho_s \mathbf{v}_s + \rho_n \mathbf{v}_n) = 0, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$\frac{\partial}{\partial t} (\rho S) + \text{div} (\rho S \mathbf{v}_n) = 0, \quad . \quad . \quad . \quad . \quad . \quad (6)$$

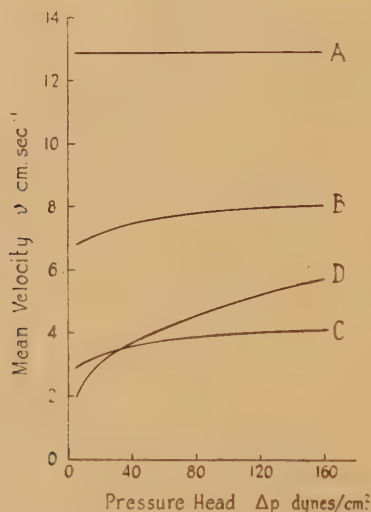
expressing conservation of mass and entropy. In addition, the boundary conditions will play as important a role as the hydrodynamical equations in determining the nature of the flow in certain experiments and, although it is normally assumed that, at a wall, $\mathbf{v}_n = 0$ and \mathbf{v}_s is unrestricted, there is no experimental foundation for this assumption. Nor can we exclude the type of complication that occurs in open gas phenomena, when the dimensions of the apparatus determine the nature of the flow in a very special way. Finally, there is the possibility that the simple two-fluid theory is a valid approximation only under certain conditions, and that under different conditions (at high velocities, for example) the division into two components breaks down completely, so that the present method of writing down two equations is then an inadequate formulation of the problem.

(b) *Flow Through the Film*

If a vessel is partially immersed in liquid helium II a thick film forms on its walls and flow takes place through this film over the rim until

the levels inside and outside the vessel stand at the same height. This phenomenon is discussed in detail in a separate article, so it will suffice to make a brief comment relevant to the present theme. Flow through the film is the nearest approximation to ideal superfluidity. The thickness of the film, d , is only about 2×10^{-6} cm, so that the flow of the viscous normal component through it is completely negligible, and it is flow of the superfluid component only that is taking place. To a first approximation, at least, the rate of flow is independent of the pressure head, suggesting the existence of a critical velocity v_c such that the frictional forces are very small, perhaps zero, below v_c , but become very large as soon as v_c is exceeded. In the film v_c has the order of magnitude of 50 cm sec^{-1} and the critical rate of flow (the product of critical velocity and film thickness $\sigma_c = v_c d$) is approximately $7 \times 10^{-5} \text{ cm}^3 \text{ sec}^{-1} \text{ cm}^{-1}$ at 1.2° K .

Fig. 4



Dependence of mean velocity on pressure head for flow through narrow channels. Temperature $= 1.2^\circ \text{ K}$. Channel widths: A, 1.2×10^{-5} cm; B, 7.9×10^{-5} cm; C, 3.9×10^{-4} cm; D, 5.0×10^{-3} cm.

(c) Isothermal Flow Through Narrow Channels

In narrow channels varying in width from 10^{-5} cm to 10^{-2} cm, there is a gradual transition from the obvious superfluidity of the film to the entirely different situation encountered in wide capillaries. There is now a definite dependence of the mean velocity of flow on the pressure head, which becomes more marked as the channel width increases. This is shown in fig. 4, which is based on the results of Allen and Misener (1939). The pressure head needed to produce a given velocity is, of course, a direct measure of the frictional forces opposing the flow, and so curves such as those in fig. 4 can be interpreted as showing how the frictional forces vary with velocity. A critical velocity is not easily defined for the wider

channels, but it is possible that the curves have a finite intercept v_c on the velocity axis and velocities of flow up to v_c would then be subject to no frictional retardation and would be truly superfluid. Above v_c , however, there is a progressive breaking down of the superfluidity as the frictional forces begin to build up in a markedly non-linear fashion as the velocity increases. As long as the channel width is less than 10^{-3} cm the flow of the viscous normal component can be neglected, and so the frictional forces being studied are those opposing the flow of the superfluid component only and, in the notation of eqn. (3), are due to $F_{sn} + F_s$ when $v_n = 0$. The most noteworthy feature is the possibility that $F_{sn} + F_s = 0$ until the critical velocity v_c is exceeded. It is clear from fig. 4 that v_c must decrease as the channel width d increases. This is consistent with an interesting suggestion made by Bijl, de Boer and Michels (1941), that v_c is determined by the quantum relationship

$$mv_c d \sim h, \quad \dots \dots \dots (7)$$

m being the mass of the helium atom. This is certainly correct in order of magnitude, but there is some evidence, both from film flow (Atkins 1950, Bowers, Brewer and Mendelssohn 1951) and flow through narrow channels (Allen and Misener 1939), that $v_c d$ is not constant but increases with d .

(d) *The Thermo-mechanical Effect*

In very narrow channels v_n is necessarily zero and, if v_s and dv_s/dt are also zero, eqn. (3) reduces to

$$-\frac{\rho_s}{\rho} \text{grad } p + \rho_s S \text{ grad } T = 0$$

or $\text{grad } p = \rho S \text{ grad } T, \quad \dots \dots \dots (8)$

which is identical with eqn. (2) for the thermo-mechanical effect. In wider channels, however, v_n cannot be neglected and the non-linear frictional forces become important; the thermo-mechanical pressure head falls below the value predicted by eqn. (8), and is no longer a linear function of the temperature difference. In these wider channels a temperature gradient is inevitably accompanied by a heat flow, and the thermo-mechanical effect becomes associated with the phenomena of thermal conduction. As explained in the introduction, thermal conduction involves a flow of the superfluid component towards the source of heat, accompanied by a counter-flow of the normal component in the opposite direction, and it can readily be shown that, when there is no resultant bulk flow of matter, the heat flow per unit area of cross-section of the channel is

$$W = \rho S T v_n = \rho_s S T (v_n - v_s). \quad \dots \dots \dots (9)$$

When the steady state is realized and the temperature difference is counterbalanced by a pressure difference so that there is no net transfer of matter ($\rho_n v_n + \rho_s v_s = 0$), v_n and v_s are not necessarily zero, but $Dv_s/Dt = Dv_n/Dt = 0$. Equations (3) and (4) may then be added to give

$$\text{grad } p = \eta_n \nabla^2 \mathbf{v}_n - F_s - F_n. \quad \dots \dots \dots (10)$$

In a channel of width d , $\nabla^2 \mathbf{v}_n$ has the order of magnitude of v_n/d^2 , and it seems that in channels of width up to 2×10^{-3} cm $\eta_n \nabla^2 \mathbf{v}_n$ is much greater than $(F_s + F_n)$, so that eqn. (10) reduces to the ordinary equation of viscous flow

$$\text{grad } p = \eta_n \nabla^2 \mathbf{v}_n, \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

which, for a parallel-sided channel, has the solution

$$\mathbf{v}_n = -\frac{d^2}{12\eta_n} \text{grad } p \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

so that

$$W = -\frac{\rho_s S T d^2}{12\eta_n} \text{grad } p. \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

This explains the experimental fact, originally discovered by Allen and Reekie (1939), that, even when the thermo-mechanical pressure is a markedly non-linear function of the temperature difference, it still varies linearly with the heat flow. Using the experimental data of Keesom and Duyckaerts (1943) and Mellink (1947) for channel widths of 19, 10.5 and 5×10^{-4} cm, values of η_n at various temperatures can be deduced from eqn. (13) and agree satisfactorily with those obtained from the oscillating disc experiments discussed in § 2(g).

(e) Thermal Conduction

Gorter and Mellink (1949) have attempted to explain thermal conduction on the assumption that $F_s = F_n = 0$ and the only important frictional term is the mutual friction F_{sn} . Eqns. (11), (12) and (13) are then true for all channel widths. Substituting from eqns. (9) and (13), eqn. (3) takes the form

$$\rho_s S \text{ grad } T = -\frac{\rho_s 12\eta_n}{\rho_s^2 S T d^2} W + F_{sn} \left(-\frac{W}{\rho_s S T} \right). \quad . \quad . \quad . \quad . \quad . \quad (14)$$

The second term on the right-hand side is independent of the channel width d , but the first term varies as $1/d^2$ and therefore becomes unimportant in wide channels so that the equation can then be written

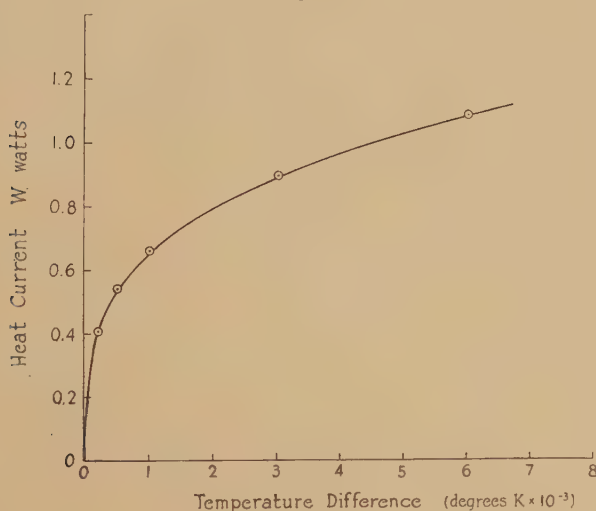
$$\rho_s S \text{ grad } T \simeq F_{sn} \left(-\frac{W}{\rho_s S T} \right). \quad . \quad . \quad . \quad . \quad . \quad (15)$$

Fig. 5 shows the results of Keesom, Saris and Meyer (1940) for thermal conduction in glass capillaries of various diameters between 0.03 and 0.16 cm. The first point to notice is that the heat current is independent of the diameter of the capillary, as would be expected from eqn. (15). Secondly, the temperature gradient varies as the cube of the heat current to a very good approximation. Gorter and Mellink therefore write F_{sn} in the form $A \rho_s \rho_n (v_s - v_n)^3$, where A is, to a first approximation, found to be independent of channel width and temperature and has a value of about 50 cm sec g⁻¹. Equation (14) then becomes

$$\rho_s S \text{ grad } T = -\frac{\rho_s 12\eta_n}{\rho_s^2 S T d^2} W - \frac{A \rho_s \rho_n}{(\rho_s S T)^3} W^3 \quad . \quad . \quad . \quad . \quad . \quad (16)$$

which can be used to explain thermal conduction in slits of intermediate width (5×10^{-4} to 2×10^{-3} cm) for which the first term on the right-hand side cannot be ignored. Fig. 6 is typical of the results obtained by

Fig. 5

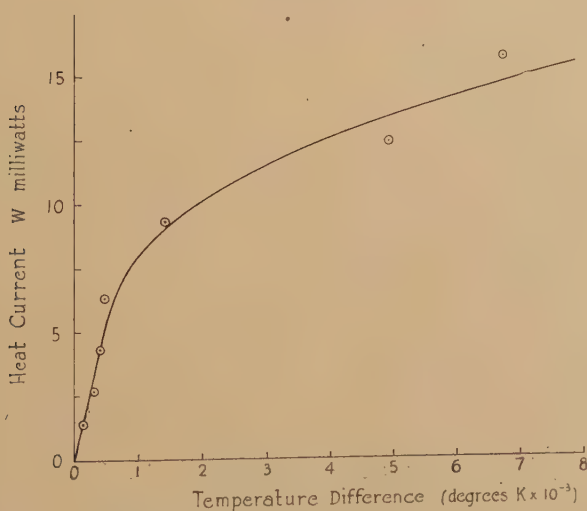


Thermal conduction in wide capillaries.

Temperature = 1.60°K .

Internal diameters of capillaries : 0.33, 0.705, 1.57 mm.

Fig. 6



Thermal conduction in a slit of width 1.05×10^{-3} cm.

Temperature = 1.72°K .

Mellink (1947), using an apparatus similar in principle to that shown in fig. 3. For small heat flows the term in W is dominant and the initial

portion of the curve is linear, but at larger heat flows the term in W^3 becomes important and the temperature difference begins to increase rapidly.

In the narrowest slits, of width 10^{-4} cm or less, the linear term always masks the term in W^3 , in agreement with the experimentally observed fact that the heat current in such slits is always a linear function of the temperature difference (Mellink and Meyer 1947). From the constant of proportionality, the effective value of η_n can be calculated, but it is found to be much smaller than the values derived by other methods, particularly at low temperatures, as is shown in table 1.

Table 1

$T^\circ \text{ K}$	$d \times 10^4 \text{ cm}$	η_n micro poise	
		Thermal conduction	Oscillating discs
2.16	1.0	5.6	19
1.09 1.66	0.5	0.08 0.9	>30 10
1.61 2.09 2.16	0.3	0.6 2.8 3.3	10.5 14 19
1.07 1.90 1.99	0.2	0.008 1.6 3.1	>30 10.5 12

Gorter and Mellink suggest that this is because the width of the slit has become comparable with, or smaller than, some mean free path which determines the viscosity. From table 1, we deduce that this mean free path would have to be much greater than 10^{-4} cm at 1.1° K and comparable with 10^{-4} cm at 2.1° K .

The hydrodynamical equations, as written by Gorter and Mellink, now take the form :

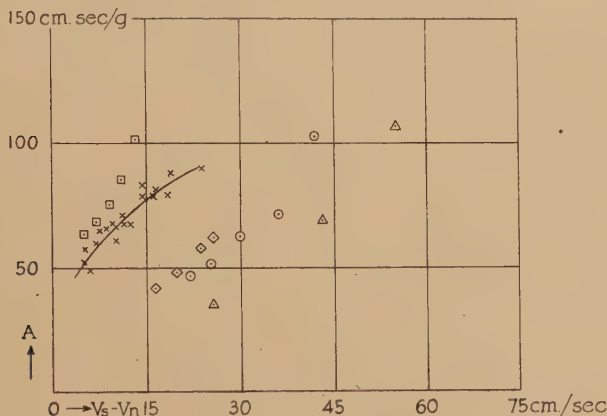
$$\rho_s \frac{D\mathbf{v}_s}{Dt} = -\frac{\rho_s}{\rho} \text{grad } p + \rho_s S \text{ grad } T - A \rho_s \rho_n (\mathbf{v}_s - \mathbf{v}_n)^3, \quad (17)$$

$$\rho_n \frac{D\mathbf{v}_n}{Dt} = -\frac{\rho_n}{\rho} \text{grad } p - \rho_s S \text{ grad } T + A \rho_s \rho_n (\mathbf{v}_s - \mathbf{v}_n)^3 + \eta_n (\nabla^2 \mathbf{v}_n + \frac{1}{3} \text{grad div } \mathbf{v}_n). \quad (18)$$

A comment should be made on the relationship between the Gorter-Mellink theory and the critical velocity theory discussed earlier. If both theories are true, then the Gorter-Mellink mutual friction must be zero until the critical velocity v_c is exceeded and must, presumably, have

some such form as $A\rho_s\rho_n[(v_s-v_n)-v_c]^3$. In the thermal experiments the values of (v_s-v_n) have been somewhat in excess of the probable values of v_c , so there is not, as yet, any reliable information on this point. In fig. 7, A is plotted as a function of v_s-v_n for various channel widths, and it will be seen that A is not quite independent of v_s-v_n , so the third power law is only approximate. For the narrower channels it is quite conceivable that the curves have a finite intercept on the velocity axis, as they should have on the critical velocity theory. Some recent results of Winkel and Hung (1951) promise to give interesting information on this point, but full details are not yet available.

Fig. 7



A as a function of $(\mathbf{v}_s - \mathbf{v}_n)$. Temperature = 2.05°K . Internal diameters of capillaries: \square 0.705 mm, \times 0.34 mm. Widths of slits: \diamond 1.9×10^{-3} cm, \circ 1.05×10^{-3} cm, \triangle 5×10^{-4} cm.

(f) Isothermal Flow Through Wide Capillaries

For steady isothermal flow under a pressure gradient the Gorter-Mellink eqns. (17) and (18) reduce to

$$\frac{\rho_s}{\rho} \text{grad } p = A \rho_n \rho_s (\mathbf{v}_n - \mathbf{v}_s)^3, \quad \dots \dots \dots (19)$$

$$\frac{\rho_n}{\rho} \text{grad } p = -A \rho_n \rho_s (\mathbf{v}_n - \mathbf{v}_s)^3 + \eta_n \nabla^2 \mathbf{v}_n. \quad \dots \dots \dots (20)$$

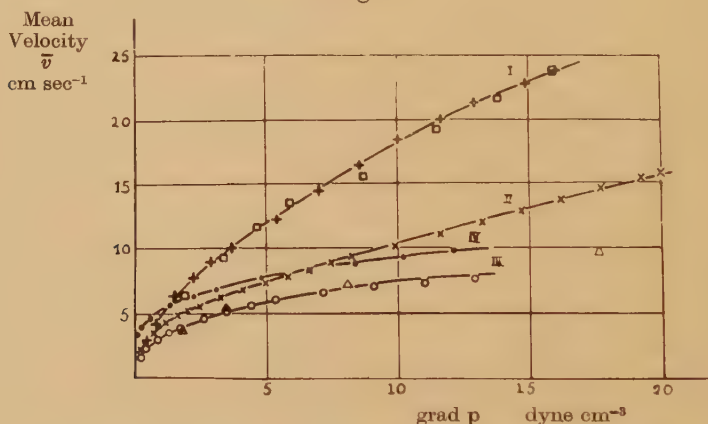
In the case of flow through a capillary of radius r , these are readily solved to give for the mean velocity of flow \bar{v}

$$\bar{v} = \frac{\rho_s}{\rho} v_s + \frac{\rho_n}{\rho} v_n = \frac{\rho_s}{\rho} \left(\frac{-\text{grad } p}{A \rho \rho_n} \right)^{1/3} + \frac{r^2 \text{grad } p}{8 \eta_n}. \quad \dots \dots (21)$$

This velocity is the sum of a Gorter-Mellink term independent of r and a viscosity term varying as r^2 . Atkins (1951) has attempted to separate these two terms by studying flow through several capillaries whose radii

ranged from 10^{-3} to 2×10^{-2} cm. A correction had to be applied for end effects which were found to result in a pressure drop of approximately $\frac{1}{2} \rho \bar{v}^2$ at each end of the capillary. A typical set of corrected results is shown in fig. 8. The critical velocity, which plays such an important part in narrow channels, is now insignificant, except perhaps in the finest capillary, and most of the flow is subject to frictional forces varying with a high power of the velocity. Equation (21) is partially successful in explaining these results. For the capillary of bore 0.08 mm, the viscosity term $r^2 \text{grad } p / 8\eta_n$ is small and \bar{v} is, in fact, approximately represented by $(\rho_s/\rho)[(\text{grad } p/A\rho\eta_n)]^{1/3}$ if A is put equal to 40 cm sec g^{-1} , which is in good agreement with the value deduced from thermal conduction. The variation of \bar{v} with r cannot, however, be represented by $r^2 \text{grad } p / 8\eta_n$. The extra velocity does not vary as r^2 and the values deduced for η_n exceed the accepted values by as much as a factor of four. It seems that the Gorter-Mellink theory is not a complete description of the flow phenomena.

Fig. 8



Flow through wide capillaries. Temperature = 1.22°K . Internal diameters :
 I, 4.40×10^{-2} cm ; II, 2.03×10^{-2} cm ; III, 0.815×10^{-2} cm ;
 IV, 0.262×10^{-2} cm.

We can, however, deduce that, if the hydrodynamics of liquid helium II is to be expressed in the form of the two eqns. (3) and (4), then the mutual friction F_{sn} must be included. If F_s were the only frictional force (apart from $\eta_n \nabla^2 v_n$) then steady isothermal flow would be described by the equation

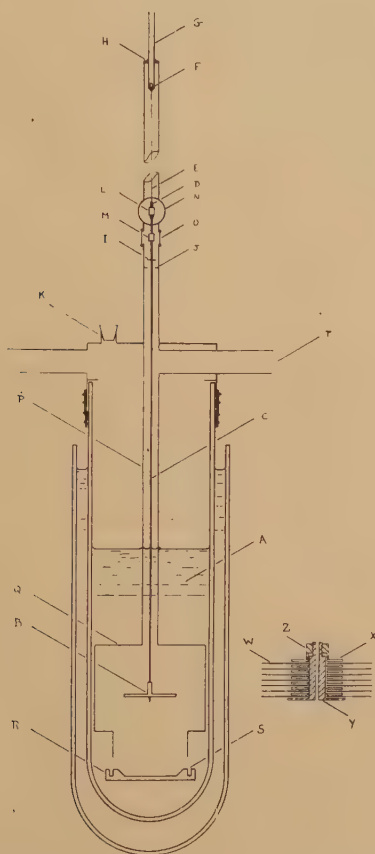
$$\frac{\rho_s}{\rho} \text{grad } p = F_s(v_s) \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

and F_s could be deduced directly from the curves of fig. 8. This value of F_s could then be used to calculate the thermal conduction, with the result that the heat current would be about 100 times greater than is actually observed. F_{sn} is therefore necessary to explain thermal conduction. We shall now consider some experiments which suggest that it is not sufficient.

(g) *Oscillating Disc Experiments*

The original two-fluid theory supposed that the damping of the torsional motion of an oscillating disc was due entirely to the viscosity of the normal component. We now see that this is likely to be true only for sufficiently small peripheral velocities of the disc and that at higher velocities the non-linear frictional forces will begin to make their contribution towards the damping. This effect was discovered by Hallett (1950, 1951, 1952). His apparatus is shown in fig. 9, and fig. 10

Fig. 9



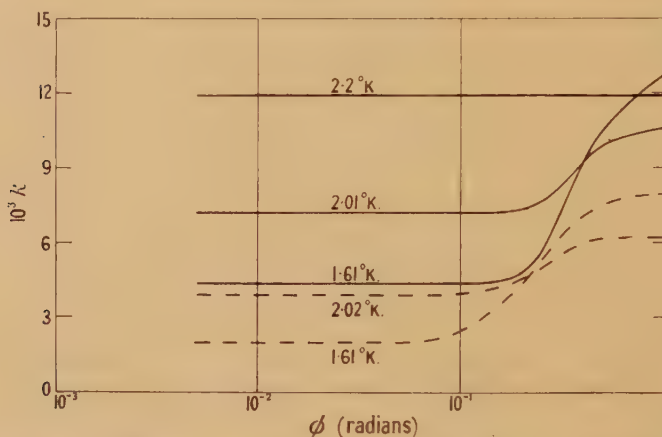
Hallett's oscillating disc apparatus.

gives some of his measurements of the logarithmic decrement as a function of the amplitude of oscillation for a single disc. Above the λ -point, at 2.2°K , the logarithmic decrement is independent of amplitude as it should be for a normal viscous liquid. Below the λ -point, the logarithmic decrement is still constant up to an amplitude of about 0.1 radian, and it is presumed that in this region the damping is due to the viscosity of the normal component alone. At amplitudes greater than 0.1 radian,

however, the extra frictional forces come into operation, the logarithmic decrement increases rapidly and then shows a tendency to saturate at a constant value in the region of 1 radian.

Hallett was able to demonstrate that this increased damping is due in some way to the superfluid component by repeating Andronikashvili's experiment with higher peripheral velocities of the discs. (See Introduction and fig. 2.) A pile of discs performed torsional oscillations in the liquid, but the period and damping were studied up to much higher amplitudes than those used by Andronikashvili. As in the case of the single disc, the logarithmic decrement remained constant at small amplitudes, and could be explained in terms of the known value of the viscosity of the normal component as deduced from the single disc experiment, but at higher amplitudes the logarithmic decrement began to increase rapidly, and the non-linear frictional forces again manifested themselves. At small amplitudes, in the region of constant decrement,

Fig. 10



Variation of logarithmic decrement with amplitude for a single disc.

Full curves for a period of 11 sec.

Dotted curves for a period of 4 sec.

the period was constant and had a value consistent with the assumption that only the normal component was contributing to the moment of inertia of the system, the values of ρ_n/ρ deduced in this way being in good agreement with those of Andronikashvili. At higher amplitudes, however, the period began to increase (fig. 11) and eventually rose to a value which suggested that the total density ρ of the liquid was moving with the discs. Here, then, is additional evidence that the superfluidity of the superfluid component is imperfect at high velocities and that, either by direct interaction with the surfaces of the discs or via an interaction with the normal component, it can then be dragged into motion with the disc system. The peripheral velocity at which the extra damping begins to appear is about 0.2 cm sec^{-1} , which puts an upper limit to the

critical velocity under these conditions. This critical velocity is with reference to a disc separation of 0.11 mm and should be compared with the critical velocity of 50 cm sec⁻¹ in the film of thickness 2×10^{-6} cm.

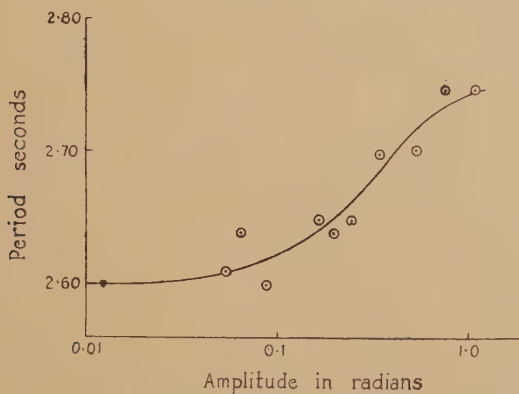
For an oscillating disc the Gorter-Mellink eqns. (17) and (18) take the form

$$\rho_s \frac{D\mathbf{v}_s}{Dt} = -A\rho_n\rho_s(\mathbf{v}_s - \mathbf{v}_n)^3, \quad \dots \dots \dots (23)$$

$$\rho_n \frac{D\mathbf{v}_n}{Dt} = +A\rho_n\rho_s(\mathbf{v}_s - \mathbf{v}_n)^3 + \eta_n \nabla^2 \mathbf{v}_n. \quad \dots \dots \dots (24)$$

These equations can be solved provided that the increase in logarithmic decrement above its value at small amplitudes is not too large. This has been done by Zwanikken (1951) for a single disc and by Hallett (1951a, 1952) for a pile of discs. The calculations are compared with the experimental results in figs. 12 and 13, which give the increase in decrement at an amplitude of 0.215 radian above its value at zero

Fig. 11

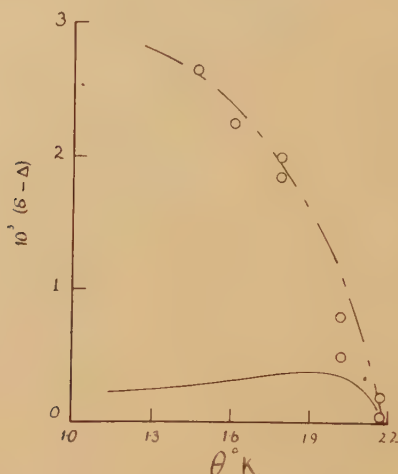


Variation of period with amplitude for a pile of discs. Temperature = 1.54° K.

amplitude as a function of temperature. The Gorter-Mellink constant A was assumed to be 50 cm sec g⁻¹, which probably makes the calculated decrement too large, as the effective value of A is likely to be much smaller at the small velocities (~ 1 cm sec⁻¹) encountered in the disc experiments than at the larger velocities (50 cm sec⁻¹) encountered in thermal conduction experiments (see fig. 7). It will be seen that the Gorter-Mellink theory is in fair agreement with experiment above 1.8° K, but that at lower temperatures there is a marked disagreement, and that at 1.2° K the theory predicts an excess decrement which is too small by a factor greater than 10. Nor does it seem possible (Hallett 1951a), to explain both the results for the single disc and the pile of discs by assuming any plausible value for A or by making the mutual friction F_{sn} a different function of $(\mathbf{v}_s - \mathbf{v}_n)$. It seems that oscillating disc experiments cannot be explained in terms of a mutual friction between

the two components and they provide strong evidence for additional frictional forces such as F_s and F_n in eqns. (3) and (4). The fact that the excess decrement increases with decreasing temperature in roughly the

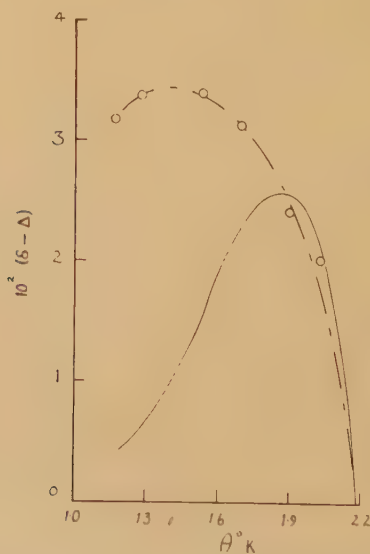
Fig. 12



Temperature variation of the excess decrement at an amplitude of 0.215 radians for a single disc.

— Gorter-Mellink theory (Zwanikken).
 - - - ρ_s scaled to fit the points.

Fig. 13



Temperature variation of the excess decrement at an amplitude of 0.215 radians for a pile of discs.

— Gorter-Mellink theory (Hallett).

same way as ρ_s (fig. 12) predisposes us to believe that the extra damping is due to a frictional force F_s inherent in the superfluid component alone.

We must consider the possibility that the increase in decrement is due to the setting in of turbulence. Turbulence occurs when the Reynolds number \mathcal{R} exceeds a certain value ($\mathcal{R} = v_m R \rho / \eta$, where v_m is the maximum peripheral velocity of the disc and R is the radius of the disc). In liquid helium I the decrement was found to remain constant up to values of \mathcal{R} equal to 50,000. In liquid helium II the Reynolds number for the normal component ($\mathcal{R}_n = v_m R \rho_n / \eta_n$) never exceeded this value, and was in some cases as low as 20 under conditions when the extra damping was well marked. Turbulence in the normal component is therefore most improbable. It is difficult to make a definite statement about the possibility of turbulence in the superfluid component. A liquid with zero viscosity might be considered highly susceptible to turbulence, and it may be that instability of the motion sets in as soon as the critical velocity v_c is exceeded. On the other hand, F. London has suggested that the behaviour of the superfluid component is described by the equation $\text{curl } \mathbf{v}_s = 0$, which suggests a reluctance to become turbulent. In any case, turbulence in the superfluid component would be an interesting and instructive phenomenon. It would, however, not require any modification of the hydrodynamical eqns. (3) and (4), merely a new type of solution of these equations.

Finally, we must take note of the results for the normal viscosity η_n which can be deduced from the damping at small amplitudes. It is important to remember that this type of experiment gives values for the product $\eta_n \rho_n$ and not the viscosity η_n directly. Before the two-fluid theory, the experiments were incorrectly interpreted as giving a viscosity $\eta = (\eta_n \rho_n) / \rho$ instead of $\eta_n = (\eta_n \rho_n) / \rho_n$. Some recent values of η_n are given in fig. 14. They were calculated using values of ρ_n derived from the velocity of second sound (§ 5 (a)), as these are believed to be the most reliable values at low temperatures. The most interesting feature is the rapid rise of η_n below 1.6°K . This will be discussed further in § 3 (c).

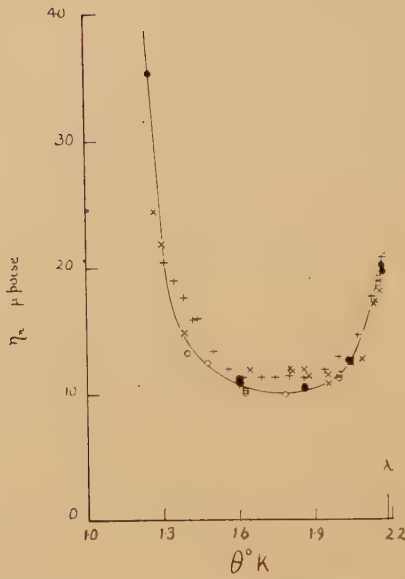
(h) *The Rotating Cylinder Viscometer*

Hallett (1951 a, 1951 b) has made a further attack on the problem, using the conventional type of rotating cylinder viscometer shown in fig. 15. The liquid was contained in the annular gap of width 1.06 mm between the two co-axial cylinders *A* and *B*, the outer of which rotated with velocities up to 3 cm sec⁻¹, while the inner was suspended by a torsion fibre. The couple transmitted through the liquid to the inner cylinder was measured by observing the angular deflection of this cylinder in the usual way. This type of arrangement has several advantages for the present purpose. It is a steady state experiment in which Dv_s/Dt , Dv_n/Dt , grad p , grad T and grad div v_n can all be ignored, so that the hydrodynamical eqns. (3) and (4) take the particularly simple form

$$F_{sn} + F_s = 0, \quad \dots \dots \dots (25)$$

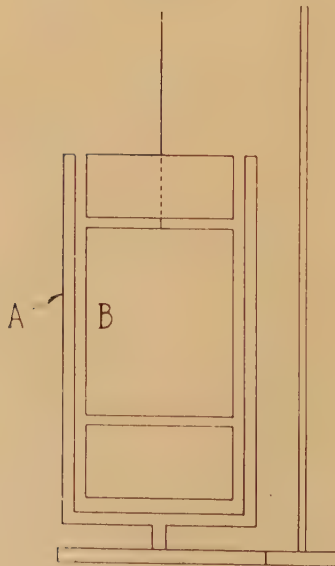
$$F_{sn} - F_n + \eta_n \nabla^2 \mathbf{v}_n = 0. \quad \dots \dots \dots (26)$$

Fig. 14



The variation of η_r with temperature.
○, single disc, $T=3.78$ sec ; ● single disc, $T=11.0$ sec ; + Andronikashvili ;
× de Troyer *et al.*

Fig. 15



The rotating cylinder viscometer.

Moreover, Taylor (1923) has shown that in this type of experiment, the flow cannot become turbulent at any velocity for a normal liquid. Finally, this experiment makes it possible to decide unambiguously whether the Gorter–Mellink theory is alone sufficient to describe the flow phenomena, for the Gorter–Mellink equations now reduce to

$$A\rho_n\rho_s(\mathbf{v}_s-\mathbf{v}_n)^3=0,$$

..... (27)

$$A\rho_n\rho_s(\mathbf{v}_s-\mathbf{v}_n)^3+\eta_n\nabla^2\mathbf{v}_n=0$$

..... (28)

from which we deduce immediately that

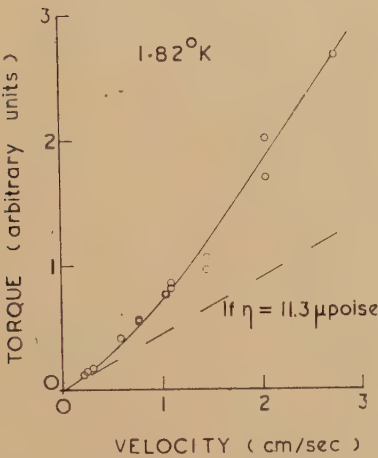
$$\mathbf{v}_s=\mathbf{v}_n,$$

..... (29)

$$\eta_n\nabla^2\mathbf{v}_n=0.$$

..... (30)

Fig. 16



The torque on the inner cylinder as a function of the velocity of the outer cylinder.

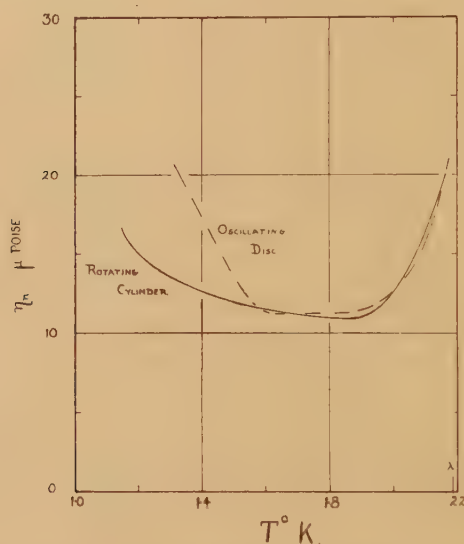
The mutual friction should therefore not influence the matter, and the method should measure merely the viscosity of the normal component.

Experimentally, however, the couple on the inner cylinder was not linearly proportional to the velocity of the outer cylinder, as it would have been for a normal viscous fluid (and was, in fact, when experiments were performed using air at room temperature and hydrogen gas at 80° K). In fig. 16 the vertical co-ordinate is proportional to the couple on the inner cylinder, and is plotted against the velocity of the outer cylinder. The dotted line is what would be expected for an ordinary viscous liquid having a viscosity equal to that of the normal component as deduced from the oscillating disc experiments. At 0.1 cm sec⁻¹ the couple is approximately that due to the viscosity of the normal component alone, but at higher velocities non-linear frictional forces set in and cannot now be explained as due to a mutual friction alone. Nor can turbulence

be adduced to explain the phenomena unless the considerations determining the stability of the motion are entirely different from those for an ordinary liquid. The experiment therefore appears to have provided irrefutable evidence for the existence of the frictional force F_s .

For small velocities of the outer cylinder, the non-linear forces can presumably be neglected and it is then possible to deduce values for the viscosity of the normal component η_n . In fig. 17 the apparent value of η_n extrapolated to zero velocity is plotted against temperature and compared with the results of oscillating disc experiments. Above 1.6 K the agreement is good, but below this temperature the rotating cylinder viscometer gives values significantly lower than those obtained from the oscillating disc. If this effect can be substantiated by further experiments, it promises to be of fundamental importance to the theory

Fig. 17



Comparison of the values of η_n obtained from oscillating disc experiments and the rotating cylinder viscometer.

of flow phenomena in liquid helium. One possible explanation has so far been suggested. The rotating cylinder viscometer gives η_n directly, whereas the oscillating disc gives $\eta_n \rho_n$ and Gorter (1951) has pointed out that the accepted values of ρ_n , which are deduced from the velocity of second sound (§ 5 (a)), may be in error at low temperatures. This might follow from Gorter's suggestion (1949) that the temperature gradient term in the hydrodynamical equations should not be $\rho_s S \text{ grad } T$ but $x(1-x)\rho(\partial S/\partial x) \text{ grad } T$, where $x = \rho_n/\rho$. Such a modification of the equations would alter the expression derived for the velocity of second sound and hence the values deduced for ρ_n .

(i) *Summary of Flow Phenomena*

Table 2 summarizes the main types of experimental evidence available on the flow of liquid helium II. Attention is drawn to the relevant dimensions and the range of velocities covered in each case, in order to emphasize the importance of these two quantities to the nature of the phenomena. For the oscillating disc the relevant dimension is taken to be the penetration depth, which is a measure of the distance through which the motion of the disc penetrates into the liquid along a normal to the plane of the disc.

Table 2

Type of experiment	Velocity range cm sec ⁻¹	Important dimensions cm	Critical velocity cm sec ⁻¹	Phenomena mainly due to
Adsorbed films	Unknown	$0 \rightarrow 2 \times 10^{-6}$	Unknown	v_c
Film in equilibrium with bulk liquid	~ 50	$\sim 2 \times 10^{-6}$	~ 50	v_c
Isothermal flow through narrow channels	$20 \rightarrow 2$	$10^{-5} \rightarrow 10^{-2}$	$20 \rightarrow 2$	$v_c, (F_{sn} \text{ and } F_s)$
Thermo-mechanical effect	$10 \rightarrow 100$	$10^{-5} \rightarrow 2 \times 10^{-3}$	—	η_n and F_{sn} Mean free path effects
Thermal conduction	$10 \rightarrow 100$	$10^{-5} \rightarrow 10^{-1}$	—	η_n and F_{sn} Mean free path effects
Isothermal flow through wide capillaries	$1 \rightarrow 25$	$10^{-3} \rightarrow 4 \times 10^{-2}$	< 1	η_n and F_{sn}
Oscillating discs	$0 \rightarrow 5$	$10^{-2} \rightarrow 0.2$	< 0.2	η_n and F_s
Rotating cylinder viscometer	$0.1 \rightarrow 3$	0.1	< 0.2	η_n and F_s

§ 3. MICROSCOPIC THEORIES

(a) *Bose-Einstein Condensation*

No microscopic theory has yet given a satisfactory explanation of superfluidity and the non-linear forces associated with its breakdown, so the discussion in the previous section had to be entirely phenomenological. However, there is much to be said about the theoretical interpretation of the experiments on first and second sound which will be described in the following pages, and so it is necessary to give a brief

introductory exposition of the two principal microscopic theories. These two theories correspond to the two different approaches to the theory of liquids in general—the liquid can be considered to be either a gas in which the interatomic forces have become large, or a solid in which the binding forces are too weak to localize the atoms near lattice-points. The first approach is embodied in the theory of Bose–Einstein condensation developed by London (1938) and Tisza (1940). Helium atoms of mass 4 contain an even number of fundamental particles and therefore obey Bose–Einstein statistics, so the basis of the theory is the application of these statistics to an ideal gas of helium atoms having the same density as the liquid. It is found that a third order transition occurs at a degeneracy temperature which is not very different from the actual temperature of the λ -point. Below this temperature a finite fraction of atoms falls into the lowest energy state, and this fraction increases with decreasing temperature until it becomes unity at 0°K . It is an obvious step to identify these atoms with the superfluid component, particularly as they have zero heat content. By introducing arbitrary assumptions about the nature of the interatomic forces, it is possible to change the transition at the degeneracy temperature into a second order one and to obtain approximate agreement with the measured specific heat data. The outstanding triumph of the theory is that it predicts that the helium atom of mass 3, which contains an odd number of fundamental particles and therefore obeys Fermi–Dirac statistics, should not show superfluidity. This isotope has shown no signs of superfluidity in experiments which have gone down to 0.25°K .

(b) *Landau's Quantum Hydrodynamics*

Landau (1941) treats liquid helium as being more analogous to a solid than a gas, and uses an approach very similar to the Debye theory of the specific heats of solids. In the Debye theory the elementary excitations, or normal modes, are taken to be longitudinal and transverse sound waves passing through the solid. Landau retains the longitudinal waves but rejects the transverse waves, because a liquid cannot support such waves (except perhaps at very high frequencies). The missing transverse waves must therefore be replaced by elementary excitations of a different kind. Landau (1947) believes that the experimental results can best be explained if the elementary excitations behave in the manner shown in fig. 18, which shows how the energy of the excitation ϵ varies with its momentum p . The elementary excitations of small energy are the longitudinal sound waves, commonly called phonons, and their energy is linearly proportional to their momentum:

$$\epsilon = u_1 p, \quad \dots \dots \dots (31)$$

u_1 being the velocity of ordinary sound. At higher values of p there is a minimum in the curve, near which

$$\epsilon = \Delta + \frac{(p - p_0)^2}{2\mu}, \quad \dots \dots \dots (32)$$

The excitations in this region are called rotons by Landau, because he suspects that they are due to rotational motions of the liquid. To justify this neat division into phonons and rotons, the thickened portions of the curve in fig. 18 indicate which excitations will be excited at a temperature of the order of 1°K . Notice that at a temperature near the λ -point (2.19°K) the rotons will begin to 'spill over' the maximum in the curve, and this will inevitably be accompanied by peculiar effects.

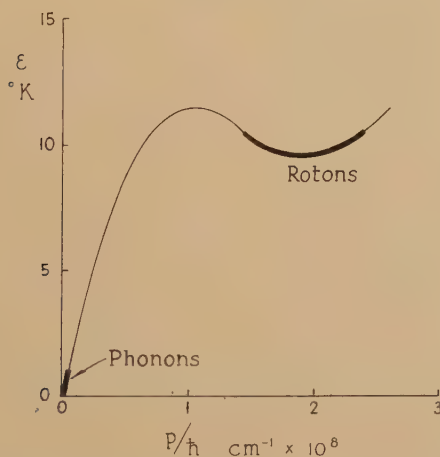
The specific heat can be expressed as the sum of two parts, due to phonons and rotons separately. The phonon contribution has the same form as in the Debye theory :

$$C_{ph} = \frac{16\pi^5}{15} \frac{k^4 T^3}{\rho \hbar^3 u_1^3} \quad \dots \quad (33)$$

The roton contribution is

$$C_r = \frac{2\mu^{1/2} p_0^2 \Delta^2}{(2\pi)^{3/2} \rho k^{1/2} T^{3/2} \hbar^3} \left[1 + \frac{kT}{\Delta} + \frac{3}{4} \left(\frac{kT}{\Delta} \right)^2 \right] e^{-\Delta/kT} \quad \dots \quad (34)$$

Fig. 18



The elementary excitations of the Landau theory.

Because of the factor $e^{-\Delta/kT}$ the roton contribution is dominant above 1°K , but can be neglected below about 0.6°K . Recently Kramers (1951) has measured the specific heat of liquid helium between 0.25°K and 0.6°K . He finds that it varies as T^3 and is in good agreement with eqn. (33), provided that only longitudinal Debye waves are counted. The specific heat above 1°K , together with the data on the velocity of second sound, is used to determine the parameters Δ , p_0 and μ .

The division into two components was established by considering a rotating cylindrical vessel full of liquid helium. From considerations of how the equations of Statistical Mechanics transform from fixed axes to axes rotating with the vessel, Landau showed that all the phonons

and rotons move with the vessel, but that the apparent moment of inertia of the rotating liquid is less than if the liquid rotated as a whole. A normal fraction ρ_n/ρ of the liquid is therefore dragged into motion by the walls of the vessel, taking with it all the elementary excitations and hence the total heat content, but leaving behind a superfluid 'residue'. From the Statistical Mechanics of the situation Landau was able to calculate ρ_n/ρ as a function of temperature. The contribution from the phonons is

$$\rho_{ph} = \frac{4}{3} \rho \frac{E_{ph}}{u_1^2} \quad \dots \quad (35)$$

where E_{ph} is the total energy of the phonons (or $\int_0^T C_{ph} dT$) which varies as T^4 . The contribution from the rotons is

$$\rho_r = \frac{2\mu^{1/2} p_0^4 e^{-\Delta/kT}}{3(2\pi)^{3/2} (kT)^{1/2} \hbar^3} \quad \dots \quad (36)$$

Above 1°K ρ_r is much greater than ρ_{ph} , but below 1°K it becomes increasingly less important until at 0.2°K only the phonons need be taken into consideration.

(c) *The Landau-Khalatnikov Theory of Viscosity*

Landau and Khalatnikov (1949) have given a discussion of the viscosity of the normal component based on the above ideas of Landau. Imagine the normal component flowing with a velocity v_{nx} in the direction of the x -axis, but with a velocity gradient $\partial v_{nx}/\partial y$ in the perpendicular direction along the y -axis. Then, at any point P the phonons and rotons have a drift velocity v_{nx} equal to the velocity of the normal component at that point—in a certain sense the phonons and rotons *are* the normal component. The phonons and rotons travel in all directions through the liquid carrying the drift momentum at the point P through a distance determined by their mean free paths. This mechanism gives rise to a viscosity in exactly the same way that the transfer of momentum by atoms is responsible for the viscosity of a gas. In fact, phonons and rotons can be treated as 'particles', in the same way that photons can sometimes be treated as 'particles', and it is possible to consider the normal component as a 'gas' of phonons and rotons. Below about 1.9°K the density of phonons and rotons is not very great and the phonon-roton gas can be treated as ideal. Above 1.9°K , however, the density of phonons and rotons is sufficiently great to make the interaction forces between them important so that the Landau-Khalatnikov theory cannot be applied in this region and cannot predict the rise in viscosity just below the λ -point.

The problem, therefore, is to calculate the efficiency of the sideways transfer of drift momentum from a consideration of the collision processes which determine the mean free paths. Transfer of momentum is due to both phonons and rotons and the viscosity can conveniently be divided into a phonon viscosity and a roton viscosity. The roton viscosity will

be considered first. Analysis of a phonon-roton collision shows that in this collision the roton plays the role of a heavy particle and the phonon that of a light particle. The 'stopping power' of a roton is therefore much greater than that of a phonon, and it is therefore justifiable to assume that an overwhelming majority of roton paths are terminated by a collision with another roton, particularly above 1°K where there is, in any case, a greater density of rotons than phonons. The roton viscosity can then be shown to take the form

$$\eta_r = \frac{1}{15} t_r N_r (p_0^2/\mu) = (\pi/10) \rho_r \bar{v}_r \lambda_r \quad (37)$$

in which t_r is the mean time between roton-roton collisions, N_r is the number of rotons per unit volume, \bar{v}_r is the mean velocity of the rotons, and λ_r is the roton mean free path. Notice that eqn. (37) is formally similar to the equation giving the viscosity of an ideal gas. Although t_r cannot be calculated directly because insufficient is known about the interaction of two rotons, it can be shown that the product $t_r N_r$ is independent of temperature, which is very plausible as the time between collisions might be expected to increase as the density of rotons decreases. As p_0 and μ are constants describing the roton, it is clear from eqn. (37) that the roton viscosity is independent of temperature—to within the approximations made in the calculations that is.

Above 1°K the phonon free paths will also be terminated, in an overwhelming majority of cases, by a collision with a roton. As the temperature decreases, the density of rotons decreases rapidly (as $T^{1/2}e^{-\Delta/kT}$) and consequently the phonon mean free path λ_{ph} increases rapidly (actually as $T^{-9/2}e^{+\Delta/kT}$). The values of λ_{ph} computed by Landau and Khalatnikov are shown in fig. 19. The phonon viscosity can be shown to have a form very similar to the expression for the viscosity of a gas:

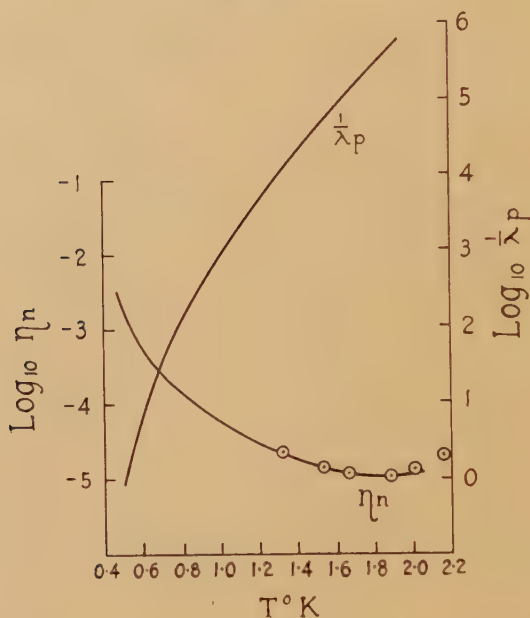
$$\eta_{ph} = \alpha \rho_{ph} u_1 \lambda_{ph}, \quad (38)$$

where α is a numerical factor which can be calculated. From eqn. (35) it can be seen that ρ_{ph} varies as T^4 and η_{ph} therefore varies as $T^{-1/2}e^{+\Delta/kT}$, explaining the rapid rise in viscosity below 1.6°K shown in fig. 14. When η_{ph} calculated in this way is subtracted from the measured viscosity η_n , the residue, which should be η_r , is found to have an approximately constant value of about 10 micro-poise between 1.3°K and 1.9°K , in accordance with the previous conclusion that the roton viscosity is independent of temperature. The values of η_n deduced from the theory are plotted in fig. 19 and compared with the results of oscillating disc experiments. The good agreement between theory and experiment may, however, be fortuitous, as the parameters needed to describe the collision processes $((\partial u_1/\partial \rho), (\partial^2 u_1/\partial \rho^2), (\partial^2 \Delta/\partial \rho^2), (\partial p_0/\partial \rho))$ are not known with any accuracy.

From Gorter and Mellink's analysis of thermal conduction experiments in channels of width 10^{-4} cm or less, it can be deduced that the mean free path is comparable with 10^{-4} cm at 2.1°K but is much greater at

1.1°K (see § 2 (e)). λ_{ph} has the right sort of behaviour to explain this, and η_{ph} might be expected to be appreciably reduced in these narrow channels. The roton mean free path, however, is certainly less than 10^{-5} cm at all temperatures above 1°K and η_r would be expected to have its full value in the narrow channels. This is not in agreement with the fact that the total viscosity under some conditions (see table 1) is appreciably less than the value of 10 micro-poise accepted above for η_r , introducing a suspicion that all is not well with the theory.

Fig. 19



The viscosity η_n and the phonon mean free path λ_p predicted by the Landau-Khalatnikov theory.

○ Andronikashvili's experimental values of η_n .

§4. FIRST SOUND

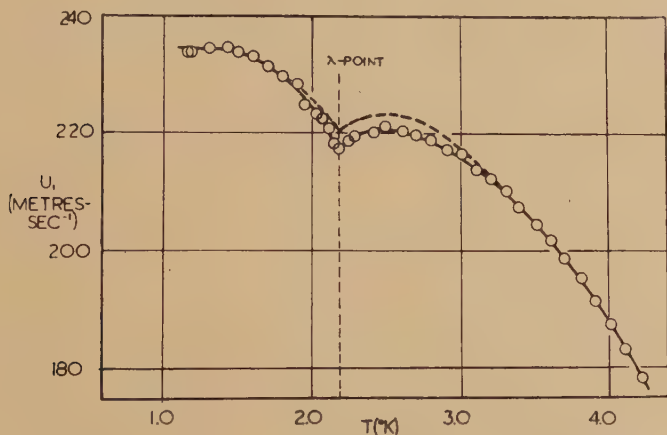
(a) Velocity of First Sound

Ordinary sound will be referred to as first sound to distinguish it clearly from second sound. The velocity of first sound has been measured by Findlay, Pitt, Grayson Smith and Wilhelm (1938) at a frequency of 1.338 mc/s, by Pellam and Squire (1947) at 15 mc/s, and by Atkins and Chase (1951) at 14 mc/s. The results are in sufficiently good agreement to indicate that the dispersion in this frequency range is certainly less than 1%. The velocity u_1 as a function of temperature is shown in fig. 20.

The behaviour of the velocity near the λ -point is interesting as it may give information concerning the nature of the λ -transition. Figure 21 shows the results of a detailed study of this region made by Atkins and Chase (1951). The conventional attitude to a λ -transition is that it is

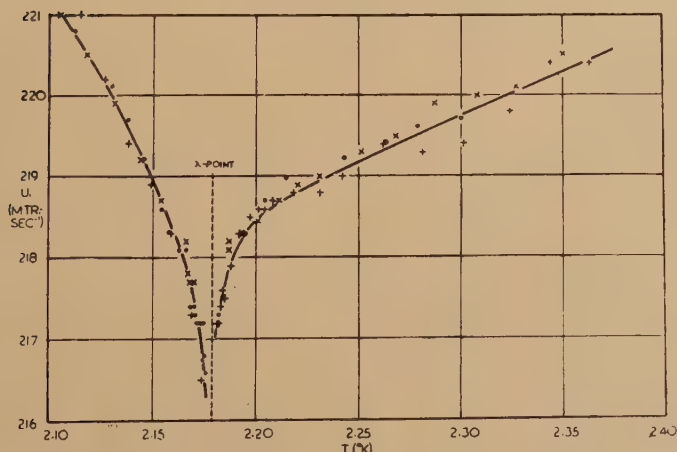
a second order transition involving discontinuities in the second derivatives of the Gibbs free energy, such as the specific heat C , the coefficient of expansion α , and the isothermal compressibility β . Ehrenfest

Fig. 20



The velocity of first sound as a function of temperature.
 - - - - - Findlay, Pitt, Grayson Smith and Wilhelm.
 -o-o-o-o-o- Atkins and Chase.

Fig. 21



The velocity of first sound in the neighbourhood of the λ -point.

has shown thermodynamically that these discontinuities can be related to one another and to the variation of transition temperature with pressure by the equations :

$$\frac{dT_{\lambda}}{dp} = \frac{TV\Delta\alpha}{\Delta C} \quad \dots \dots \dots (39)$$

$$= \frac{\Delta\beta}{\Delta\alpha} \quad \dots \dots \dots (40)$$

However, in the case of liquid helium, as in all the other cases, it is not possible to measure the discontinuities accurately because quantities like C and α are varying very rapidly in the neighbourhood of the λ -point and, as their measurement involves a small temperature decrement, it is difficult to measure them sufficiently near the λ -point to extrapolate the measured values to the λ -point itself. The velocity of first sound can be measured with considerable accuracy at a spot temperature, but there is the new difficulty that the velocity is given by

$$u_1^2 = \left(\frac{\partial \rho}{\partial p} \right)_S \quad \dots \quad (41)$$

$$= \gamma \left(\frac{\partial \rho}{\partial p} \right)_T \quad \dots \quad (42)$$

$$= -\frac{\gamma V}{\beta},$$

involving the isothermal compressibility β and the ratio of the specific heats γ , both of which vary very rapidly near the λ -point. However, it can be shown, using the Ehrenfest relations, that the behaviour of γ cannot mask a discontinuity in β , and, on the basis of the values at present accepted for the discontinuities in C and α , one might expect a $2\frac{1}{2}\%$ discontinuity in u_1 . Unfortunately, the variation of u_1 near the λ -point is so rapid that it is obviously still impossible to make a reasonable extrapolation and deduce anything about this discontinuity. The only hope is that more accurate measurements of α , from which γ can be calculated ($\gamma - 1 = T u_1^2 \alpha^2 / C_v$), will enable the isothermal compressibility β to be deduced and that this will behave in a more reasonable fashion.

Recently Tisza (1949) has suggested that all this may be not so much a difficulty as a significant feature of λ -transitions, and that these transitions are characterized, not by a discontinuity in the second order derivatives of the Gibbs free energy, but by some of these derivatives becoming infinite. This is quite possible, for in a two-dimensional model of a ferromagnetic treated by Onsager (1944), the specific heat becomes infinite at the transition temperature. Figure 21 might be explained by the assumption that the compressibility β tends to infinity at the λ -point and that u_1 therefore tends to zero. The specific heat data (fig. 22) is likewise consistent with the possibility that the specific heat is infinite at the λ -point. It is obviously important to make a thorough examination of all the relevant quantities near the λ -point, to see if there is any clear-cut case of a discontinuity or whether they all tend to zero or to infinity.

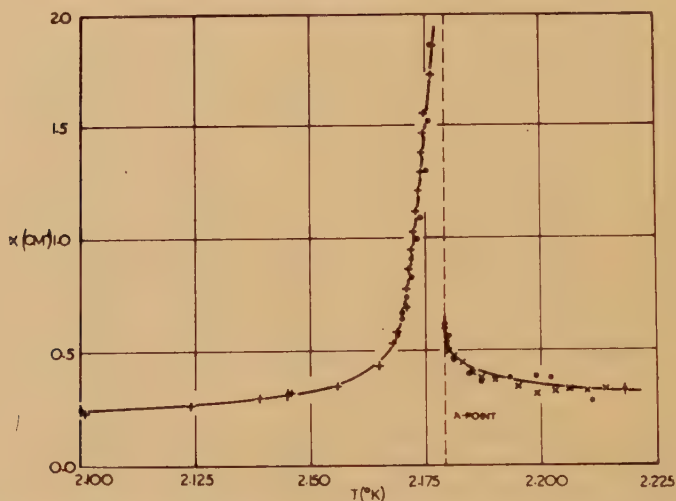
(b) Attenuation of First Sound

Figure 23 shows the data of Atkins and Chase on the attenuation at 14 mc/s. It is in substantial agreement with the earlier data of Pellam and Squire at 15 mc/s which, however, did not include temperatures

K is the thermal conductivity and ν , of course, the frequency. These classical formulae give a satisfactory explanation of the attenuation above 3°K , but the increase in attenuation near the λ -point and the rapid rise below 2.0°K are effects due to the peculiar nature of liquid helium.

Figure 24 is an enlargement of the region near the λ -point. The only detailed attempt to explain this increased attenuation is due to Pippard (1951) who ascribes it to fluctuation effects. He visualizes the liquid just above the λ -point as a matrix of He I containing small inclusions of He II. Because the coefficient of expansion is positive for He I but negative for He II, the compressions due to the sound wave warm the matrix but cool the inclusions. Heat is then transferred from the matrix

Fig. 24

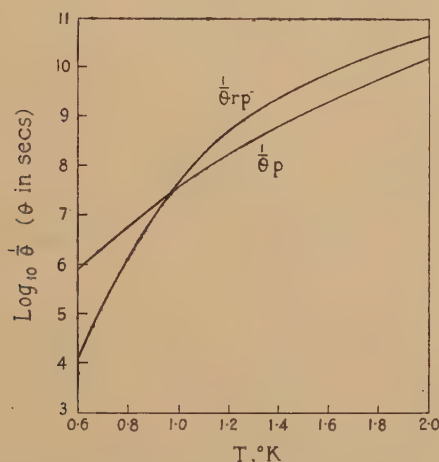


The attenuation of first sound in the neighbourhood of the λ -point.

to the inclusions with a characteristic relaxation time, and there results the type of attenuation which is always associated with relaxation effects. Moreover, the cooling effect of the inclusions implies that the temperature rise in the matrix will be reduced, the situation will be intermediate between the ideal isothermal and adiabatic cases and the effective value of γ will be decreased. This is advanced as the explanation of the sharp decrease in the velocity as the λ -point is approached from above. Pippard is able to show that this mechanism predicts the correct order of magnitude for the anomalous attenuation above the λ -point, but an exact calculation proves to be very difficult. An essential assumption in the theory is that the anomalous behaviour of the specific heat just above the λ -point is also due to fluctuations, and this in itself is a sufficiently important point to merit a rigorous statistical proof.

The rapid rise in attenuation below 2°K was predicted by Khalatnikov (1950) before its discovery. The dotted curve in fig. 23 shows how well his prediction was verified by experiment. The basic mechanism in the Khalatnikov theory is somewhat similar to the relaxation effect which gives rise to the anomalous absorption of sound in a diatomic gas, when the rotational and vibrational energy levels of the molecules are not able to adjust themselves immediately to the changes in temperature accompanying the adiabatic compressions and rarefactions of the sound wave. When liquid helium II is compressed adiabatically, the number of rotons and phonons present has to adjust itself to the new conditions of density and temperature, but can only do so after a characteristic relaxation time determined by those collision processes which create new phonons and rotons. Whereas in the Landau-Khalatnikov theory of viscosity it was necessary to consider only the *elastic* collisions tending to

Fig. 25



The relaxation times of Khalatnikov's theory.

equalize the momentum throughout the phonon-roton gas, it is now necessary to consider *inelastic* collisions during which phonons and rotons are absorbed and emitted. The two relaxation times associated with the two most important processes are plotted against temperature in fig. 25. θ_p results from collisions in which two incident phonons produce three scattered phonons. θ_{rp} results from collisions in which two incident rotons produce a single roton and a high energy phonon, or the reverse process in which a collision between a roton and a high energy phonon results in two scattered rotons. It will be seen that, above 1°K , the reciprocal of the relaxation time ($\sim 10^9$) is large compared with the frequency used in the experiment ($\sim 10^7$), and so the experiments fall within the frequency range where the absorption is proportional to the

square of the frequency ν . The absorption coefficient α_1 can therefore be written in the form

$$\alpha_1 = \frac{2\pi^2\nu^2}{\rho u_1^3} \left(\frac{4}{3}\eta_n + \zeta_I \right) \quad . \quad . \quad . \quad . \quad . \quad . \quad (45)$$

where η_n is the coefficient of ordinary viscosity (first viscosity) and ζ_I , the coefficient of second viscosity, results from the relaxation effects. ζ_I can be calculated except for two parameters and the values of these parameters used by Khalatnikov to deduce the dotted curve in fig. 23 had to be derived from the earlier results of Pellam and Squire (1947) on the absorption in the temperature range 1.6° K to 2.0° K. At all temperatures above 1° K ζ_I exceeds η_n by a factor of the order of 10.

Although the Khalatnikov theory gives large absorptions, it does not predict any appreciable dispersion. The change in velocity between zero frequency and infinite frequency is given as a function of temperature in table 3, and it will be seen that the dispersion is never greater than 1% ($u_1 \sim 2 \times 10^4$ cm sec⁻¹).

Table 3

$T^\circ \text{ K}$	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4	1.5	1.6	1.7	1.8	1.9	2.0
$\frac{u_{1\infty} - u_{10}}{\text{cm sec}^{-1}}$	0.175	1.45	5.80	13.5	23.0	37.5	51.0	73.5	90.5	115	140	165	195	240	275

Finally, we notice that the 'classical' absorption dependent on η_n is already complicated at 1.2° K by the fact that the wavelength at 14 Mc/s is 1.7×10^{-3} cm, which is comparable with the phonon mean free path λ_p (fig. 19).

§ 5. SECOND SOUND

(a) *The Nature of Second Sound*

We saw in § 2 (a) that the hydrodynamical situation in liquid helium II is described by the two eqns. (3) and (4) for the two components separately, plus the two subsidiary conditions of eqns. (5) and (6). It can be shown that these four equations lead to two distinct types of wave propagation known as first and second sound. First sound is ordinary sound with a velocity u_1 given by

$$u_1^2 = \left(\frac{\partial p}{\partial \rho} \right)_S \quad . \quad . \quad . \quad . \quad . \quad . \quad (41a)$$

and it involves oscillations of both components in phase with one another resulting in a periodic variation of the density at any point fixed in the liquid. Second sound is a thermal wave with a velocity u_2 given by

$$u_2^2 = \frac{\rho_s}{\rho_n} \frac{TS^2}{C} \quad . \quad . \quad . \quad . \quad . \quad . \quad (46)$$

and it involves oscillations of the two components in opposite directions in such a way that the density of the liquid remains unaltered, but the concentration of the normal component increases at one point while the

concentration of the superfluid component increases at a point half a wavelength away. As the normal component is 'hot' and the superfluid component 'cold', this results in a temperature oscillation being propagated through the liquid with a velocity u_2 . An instructive way of looking at second sound is to regard it as a 'density wave' in the phonon-roton gas, for an increase in the number of phonons and rotons per cm^3 at any point does not change the actual density ρ of the liquid, but does raise the temperature at that point.

Second sound was predicted by Tisza (1940) and Landau (1941) and first observed by Peshkov (1946). He excited it by passing an alternating current through a constantan wire wound backwards and forwards across the plane face of a disc-shaped former. As the thermal capacity of such a wire is very low at helium temperatures, the temperature of the wire was able to follow the periodic variation in Joule heat and the resulting temperature variation was propagated through a tube containing liquid helium II, and received on a phosphor bronze resistance thermometer similarly wound on a plane former. A steady current passed through the resistance thermometer so that the periodic variation in its resistance produced an alternating voltage which was amplified and then displayed on the screen of a cathode ray oscilloscope. When the distance between transmitter and receiver was varied nodes and antinodes were observed, and the velocity deduced from the wavelength in the usual way. Above 1°K all the quantities on the right-hand side of eqn. (46) are known— S and C from specific heat measurements and ρ_s and ρ_n from Andronikashvili's oscillating disc experiment. It was therefore possible to verify that eqn. (46) does in fact give an accurate representation of the velocity of second sound. Actually this equation is now commonly used to derive values of ρ_s and ρ_n , as it is believed to be more accurate than Andronikashvili's method below 1.6°K .

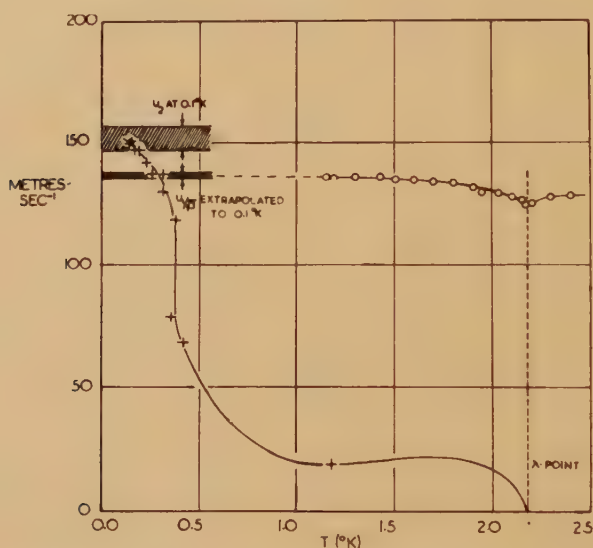
A radar-type pulse technique has been developed by Pellam (1949) and by Osborne (1951) to investigate second sound. They feed a square pulse of current into the transmitter and display on their oscilloscope screen both this input pulse and the pulse arriving some time later at the receiver. From the time delay they can deduce the velocity, and by studying the variation in height and shape of the pulse as the path length is varied, they can investigate attenuation effects. Apart from its convenience, this method has the advantage that it reduces the total heat fed into the transmitter.

(b) *Second Sound Below 1°K*

The behaviour of second sound below 1°K provides a very crucial test of the correctness of some of Landau's views and their relationship to the theory of Bose-Einstein condensation. Above 1°K , u_2 rises from zero at the λ -point to a maximum value of $20.3 \text{ metres sec}^{-1}$ ($\sim u_1/10$) near 1.65°K and then slowly falls. Tisza and London, on the basis of the theory of Bose-Einstein condensation, predicted that this fall should

continue below 1°K and that the velocity should tend to zero at 0°K as $T^{1/2}$. Landau, on the other hand, predicted that the velocity should begin to rise again and should approach the value of $u_1/\sqrt{3}$ at 0°K . In a series of experiments it became increasingly more apparent that Landau's view was the correct one. Peshkov (1948) and Maurer and Herlin (1949) investigated the region near 1°K and found that the velocity goes through a minimum and begins to rise again rapidly. Pellam and Scott (1949) used an adiabatic demagnetization technique to reach still lower temperatures and measured velocities up to $33.9 \text{ metres sec}^{-1}$. Finally, Atkins and Osborne (1950) extended the measurements down to 0.1°K , where the velocity was found to level out to a value of

Fig. 26



The velocity of second sound as a function of temperature.

—+—+—+—+—+— u_2 (Atkins and Osborne 1950).

—o—o—o—o—o— $\frac{u_1}{\sqrt{3}}$ (Atkins and Chase 1951).

approximately $152 \text{ metres sec}^{-1}$, which is very close to the value of $1/\sqrt{3}$ times the velocity of first sound predicted by Landau. The complete curve is plotted in fig. 26, which also includes a plot of $u_1/\sqrt{3}$ and its suggested extrapolation to 0°K . The shaded areas represent the authors' estimates of the experimental errors involved in both cases. There is obviously some evidence that u_2 is slightly greater than $u_1/\sqrt{3}$ near 0.1°K , but this will be disregarded at the moment as involving, at the most, a refinement of Landau's theory, and we will consider the significance of the fact that u_2 is very nearly equal to $u_1/\sqrt{3}$.

Landau's argument can be reproduced very simply. At sufficiently low temperatures rotons are unimportant and only phonons need be considered. We can therefore write

$$S = \alpha T^3, \quad (47)$$

$$C = 3\alpha T^3, \quad (48)$$

$$E = \frac{3}{4}\alpha T^4, \quad (49)$$

$$\rho_n = \frac{4}{3}\rho \frac{E}{u_1^2} = \frac{\rho\alpha T^4}{u_1^2}, \quad (50)$$

$$\rho_s \rightarrow 1. \quad (51)$$

Equation (46) for the velocity of second sound therefore becomes

$$u_2^2 = \frac{\rho u_1^2}{\rho\alpha T^4} \frac{T(\alpha T^3)^2}{3\alpha T^3},$$

$$u_2^2 = \frac{u_1^2}{3}. \quad (52)$$

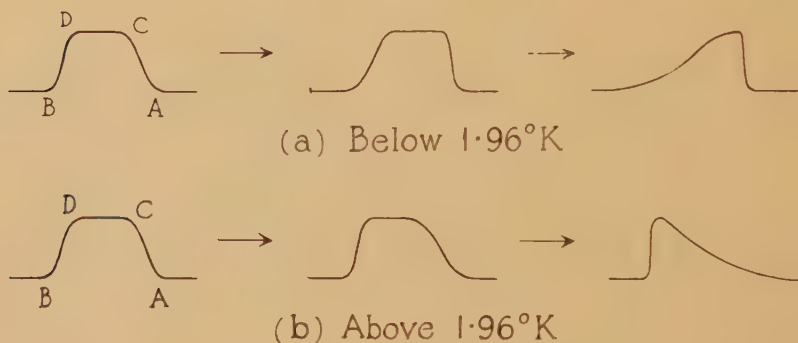
Two aspects of the theory essential to this argument must be emphasized. The first is the assumption that the low energy elementary excitations are phonons, and that they must be included in the normal component and not, as was once suggested, in the superfluid component. The second is the very special argument used by Landau to express ρ_n in the form given in eqn. (35). The bearing of the experimental result on the Bose-Einstein theory is complicated by the fact that some of the earlier predictions made by the exponents of this theory were based on erroneous *ad hoc* assumptions not essential to the theory. However, Temperley (1951a) and Dingle (private communication) have helped to clarify the situation. It seems that the theory of Bose-Einstein condensation will give a non-zero value of u_2 at 0°K only if it is supplemented by Landau's special method of calculating ρ_n . Even then the theory for an ideal gas still gives $u_2 \propto T^{1/2}$ near 0°K , and so it is essential to take interatomic forces into account. The desired result can then be obtained only if we assume that the energy ϵ of an atom in the liquid is related to its momentum p by $\epsilon = u_1 p$. Such a drastic modification of the relationship $\epsilon = p^2/2m$ applicable to the ideal gas emphasizes the importance of the interatomic forces, and it could be argued that so radical a departure from the 'gas-like' condition is a strong argument in favour of Landau's approach from the 'solid-like' condition.

(c) Shock Waves of Second Sound

Before discussing attenuation, it is necessary to consider the complication which arises from the shock wave effects discovered by Osborne (1951). Consider the propagation of a pulse with a finite time of rise and fall such as that shown in fig. 27, which is a picture in space of the pulse as it travels through the liquid. Because the hydrodynamical

equations are non-linear, it can be shown (Temperley 1951 b) that the effective velocity of propagation of the top of the pulse CD is not u_2 but $u_2 + v_s + v_n$, where v_s is the velocity of the superfluid component, which is in the opposite direction to u_2 and is therefore negative, and v_n is the velocity of the normal component in the same direction as u_2 and therefore positive. Below 1.96°K v_n is greater than v_s , and the velocity of the top of the pulse CD is therefore greater than the velocity u_2 of its leading foot A and trailing tail B . The result of this is that the leading edge AC becomes steeper while the tail DB lengthens. Eventually a steep shock front is formed and travels with a velocity $u_2 + \frac{1}{2}(v_s + v_n)$. Conditions in this shock front probably result in attenuation of the maximum amplitude. Osborne was able to demonstrate this change in shape of the pulse and to show that the velocity was in fact increased when the shock front developed. An interesting effect was observed above 1.96°K when

Fig. 27



Shock wave effects in second sound.

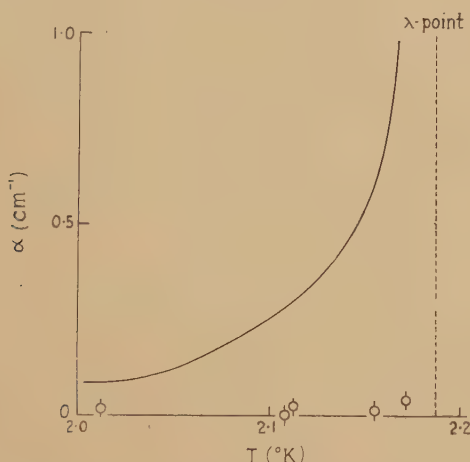
v_s became greater than v_n and the top of the pulse CD travelled more slowly than A and B . The leading edge was then observed to lengthen while the rear of the pulse became steeper. When studying attenuation of second sound, it is obviously important to avoid these shock wave effects, and this means working with very small pulses for which $|v_s + v_n| \ll u_2$.

(d) *The Attenuation of Second Sound*

The subject of attenuation of second sound is marked by a scarcity of experimental evidence and a multiplicity of possible mechanisms suggested by the theoreticians. Above 1°K the attenuation has been measured by Pellam (1949) and by Osborne (1954), both using a pulse technique and observing the decrease in pulse height at increasing distances from the transmitter. Their results are shown in fig. 28 and are in obvious disagreement. This may be due to the complicating influence of shock wave effects which become very important near the

λ -point where v_s becomes very large. Alternatively, the attenuation may increase with frequency in which case its effect would be to increase the rise time of the pulse without altering the amplitude of the flat top to which the pulse eventually rises. The lower attenuations observed by Osborne may have been a consequence of the fact that his pulses were longer than those of Pellam and therefore rose more nearly to their flat top.

Fig. 28

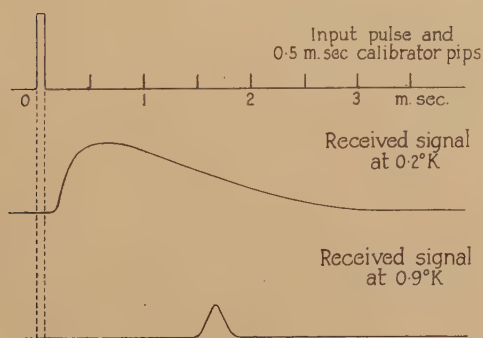


The attenuation of second sound near the λ -point.

Full line : Pellam, pulse length = 150μ sec.

Circles : Osborne, pulse length = 600μ sec.

Fig. 29



The distortion of second sound pulses below 1°K .

In the investigations of Pellam and Scott (1949) and Atkins and Osborne (1950), below 1°K the received pulses were observed to be appreciably rounded and lengthened. The effect is shown in fig. 29 and it implies the existence of dispersion accompanied, no doubt, by

attenuation. It is improbable that shock wave effects were important in this case, because the pulse shape and velocity were found to be independent of amplitude.

The attenuation mechanisms which have been suggested will be listed with only slight comment, and no attempt to judge them on the basis of the meagre experimental data. Shock wave effects have already been discussed. Gorter and Mellink (1949) suggest that their mutual friction $A\rho_n\rho_s(v_s-v_n)^3$ should give rise to attenuation in a second sound wave in which the two components are moving in opposite directions. The decay of the amplitude would not be exponential, but would be more marked at higher amplitudes because of the dependence of the friction on the third power of the amplitude. Unfortunately, the effect is likely to become important at just those amplitudes where shock wave effects set in. The theory of Khalatnikov (§ 4(b)) is applicable to the attenuation of second sound as well as first sound. For the coefficient of attenuation of second sound he obtains

$$\alpha_2 = \frac{\omega^2 \rho_s}{2\rho\rho_n u_2^3} \left[\frac{4}{3}\eta_n + \zeta_{II} \right]. \quad (53)$$

The present coefficient of second viscosity ζ_{II} is not the same as the coefficient ζ_I encountered in the case of first sound. Above 0.6° K , at least, the major contribution is from η_n and the relaxation effects determining ζ_{II} are not very important. As the relevant frequencies in the experiments were very low ($< 10 \text{ K/cs}$) the attenuation due to α_2 could not have been detected above 1° K , except perhaps very near the λ -point where u_2 is tending to zero. Below 1° K α_2 increases rapidly because η_n is increasing and ρ_n is decreasing, and this might well be the explanation of the observed pulse distortion. We notice, however, that we again run into the complication that the mean free path becomes large below 1° K and soon becomes comparable with the wavelengths involved in the second sound. Moreover, as the second sound was propagated along a tube, the dimensions of this tube may be important in comparison with the mean free path. Dingle (1950) independently gives a formula similar to eqn. (53), and also discusses the effects of 'normal' thermal conductivity (not due to a counterflow of the two components) and viscous and thermal effects due to the walls of the tube through which the second sound is propagated. None of these effects seems very important above 1° K , but all might conceivably become important below 1° K .

(e) *The Discrepancy Between u_2 and $u_1/\sqrt{3}$*

Figure 26 suggests that near 0.1° K u_2 is approaching a value about 10% greater than $u_1/\sqrt{3}$. This may be due to dispersion of second sound or first sound, or both. Landau's prediction compares second sound of zero frequency at 0° K with first sound of zero frequency at 0° K . The experiments compare second sound of uncertain frequency at 0.1° K with first sound at a frequency of $1.4 \times 10^7 \text{ c/s}$ and a temperature of 1.2° K ,

The possibility of dispersion in first sound will be considered on the basis of what is known at present about its attenuation. At 0.1°K the only important elementary excitations in the theory of second sound are phonons, and they have an average frequency of $kT/h = 2 \times 10^9$ c/s. The point at issue, then, is whether the phonons of frequency 2×10^9 c/s have the same velocity as that measured at a frequency of 1.4×10^7 c/s and a temperature of 1.2°K . Although the relaxation effects discussed by Khalatnikov (§ 4(b)) result in large attenuations, they do not lead to any appreciable dispersion (table 3). There remains the attenuation due to viscosity of the first kind, η_n . As η_n is increasing rapidly below 1°K (fig. 14), this attenuation becomes quite large, but is limited as soon as the wavelength of the first sound becomes less than the mean free path. There is, therefore, no clear indication that η_n will ever lead to a measurable dispersion. Thus no mechanism is yet available to produce the necessary dispersion in first sound. In this connection, it should be noticed that dispersion of phonons is implicit in the curvature near the origin of the curve of fig. 18, and that such a dispersion is essential to the theory of phonon-phonon collisions as contained in the Landau-Khalatnikov theory of viscosity (§ 3(c)). However, the dispersion which is assumed in this theory is only 1 part in 10^5 between zero frequency and 2×10^9 c/s and is negligible from the present point of view.

A much better case can be made out for dispersion of second sound. In fact, the pulse distortion observed below 1°K (fig. 29) provides an experimental proof of it. The velocity u_2 was obtained from the oscillograms of fig. 29 by measuring to the foot of the received pulse, but it cannot be assumed that the velocity measured in this way refers to zero frequency. The dispersion might be of such a nature that the high frequencies have a greater velocity than the low ones and are therefore received first. Dingle (private communication) has shown that this occurs, for example, when square pulses are attenuated by viscous forces. Too high a value of u_2 obtained in this way would provide a satisfactory explanation of the 10% increase of u_2 above $u_1/\sqrt{3}$.

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*Properties of Helium Three at Low Temperatures**

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§ 1. NATURAL SOURCES OF HELIUM THREE

THE existence of a stable isotope of helium of mass three was first experimentally demonstrated by Alvarez and Cornog (1939 a and 1939 b). Using helium gas in a cyclotron they were able to accelerate the 'light alpha-particle', as they called it, and to observe it by placing a counter in the ion beam. In their experiments they employed helium gas from two sources, namely: (a) so-called 'well-helium', obtained from the U.S. Bureau of Mines natural gas well at Amarillo, Texas, (The Cliffside Well) and (b) atmospheric helium obtained as a by-product from the liquefaction and rectification of air. Their results indicated that the relative abundance of ^3He in ^4He differed in the gases from the two different sources, being given approximately by the ratio $(^3\text{He}/^4\text{He})_{\text{atmos}} : (^3\text{He}/^4\text{He})_{\text{well}} = 12 : 1$. The absolute magnitude of the abundance of ^3He in the gas from any one source could not be obtained with the same degree of accuracy, but was estimated to be $(^3\text{He}/^4\text{He})_{\text{atmos}} \approx 10^{-7}$, a figure which was subsequently shown to be a factor of ten too small.

* Assisted by a contract between the United States Atomic Energy Commission and the Ohio State University Research Foundation.

More accurate measurements of the abundance of ^3He in ^4He have subsequently been made, notably by Aldrich and Nier (1946) and by Coon (1949). Aldrich and Nier used a mass spectrograph of high resolution in which the ^3He peak was clearly resolved from the HD peak, a necessary requirement in the measurement of such very small abundances of ^3He . Their results which have been confirmed by many subsequent mass-spectrographic measurements are given in table 1. The more recent measurements of Coon involved the observation of the rate of nuclear reaction of ^3He when the gas was placed in a known slow neutron flux. ^3He has a large cross section for thermal neutrons (5000 barns for 293°K neutrons (Coon and Nobles 1949, King and Goldstein 1949, Batchelor, Epstein, Flowers and Whittaker 1949)), yielding the reaction $^3\text{He}(n, p)^3\text{H}$. The experiment therefore consisted in putting the helium gas under test in a proportional counter located in a region containing thermal neutrons and counting the rate of the ^3He disintegrations. Calibration of the counter and of the neutron flux was made by substituting ^{14}N for the helium and counting the disintegration rate for well known reaction $^{14}\text{N}(n, p)^{14}\text{C}$. The results for the abundance of ^3He in ^4He , obtained in this way for both well-helium and for atmospheric helium were within experimental error the same as those reported earlier by Aldrich and Nier.

Table 1. Natural Abundance of ^3He

<i>Gas</i>	$^3\text{He}/^4\text{He}$
(a) Well-helium	1.4×10^{-7}
(b) Atmospheric helium	12×10^{-7}

The discrepancy between the measured abundance of helium three in well-helium and in atmospheric helium is of considerable interest and has prompted further work on helium obtained from other sources. Aldrich and Nier (1948) have measured mass-spectrographically the occurrence of ^3He in various natural sources of helium. Their experimental survey included observations on helium from radioactive ores, from beryl which was shown by Strutt (1907) to be unusually rich in helium, from spodumene and from a number of natural gas wells. No attempt was made to sample atmospheric helium from air at different altitudes or locations, but in view of the experimental result obtained by Gluckauf and Paneth (1946), namely that the abundance of ^4He in air from different sources was invariant, such investigations would not appear profitable. A table showing the main results of Aldrich and Nier is given in table 2, in which it will be seen that (a) essentially no ^3He occurs in the radioactive ores, (b) beryl and spodumene, which are not radioactive, contain ^3He in varying abundance up to 120×10^{-7} and (c) that helium from gas wells shows considerable scatter in the value of the ^3He abundance from 0.5 to 5.0×10^{-7} .

The occurrence of ^3He , as evidenced by the experiments outlined above, with abundance markedly dependent on the location and nature of the source presents an interesting problem of interpretation. It might be

mentioned parenthetically here that the other rare isotopes of helium, ^5He and ^6He , being unstable, need not be considered in this problem. ^5He has not been observed in spite of the fact that in their work both Alvarez and Cornog (1939 a) and Aldrich and Nier (1948) made a careful search for it. The calculated mean life time for ^5He is 2.4×10^{-21} seconds. (Hornyak, Lauritsen, Morrison and Fowler 1950.) ^6He can be produced by the reaction $^9\text{Be}(n, \alpha)^6\text{He}$, as was first shown by Bjerger (1936), and it decays to ^6Li by β -particle emission with a half life time of 0.85 seconds.

Table 2. Natural Abundance of ^3He as found by Aldrich and Nier (1948)

Mineral	Location	($^3\text{He}/^4\text{He}$) $\times 10^7$
<i>Radioactive Ores</i>		
Blomstrandine	Hittero, Norway	0.2
Pitchblende	Great Bear Lake, Canada	0.3
Monazite	Bahai, Brazil	0.2
Uraninite	Joachimsthal, Czechoslovakia	0.3
<i>Non-radioactive Ores</i>		
Beryl	Lemnas, Kimito, Finland	0.5
Beryl	Jokkmokk Parish, Lapland, Sweden	1.8
Beryl	West Rumney, New Hampshire, U.S.A.	12.0
Spodumene	Edison Mine, South Dakota, U.S.A.	120.0
<i>Gas Wells</i>		
Natural gas well	Rattlesnake Well, New Mexico, U.S.A.	0.5
Natural gas well	Cliffside Well, Amarillo, Texas, U.S.A.	1.4
Natural gas well	Gulf Oil, W. Grimes Well, Lea County, New Mexico, U.S.A.	5.0

In 1941 Hill (1941) suggested that the occurrence of helium three both in the earth's crust and in the atmosphere could be due to the transformation of ^6Li in the lithosphere by neutron bombardment. The reaction $^6\text{Li}(n, \alpha)^3\text{H}$, which was studied in detail for example by Livingston and Hoffman (1938), yields ^3H (Tritium), which decays to ^3He by β -particle emission with a half life of 12.5 years. (Jenks, Ghormley and Sweeton 1949, see also Hornyak, Lauritsen, Morrison and Fowler 1950.) Hill supposed that for the production of ^3He the bombarding neutrons were those associated with cosmic radiation and thus was able to make an estimate of the resulting ^3He abundance. It is probable, however, that this mechanism is by itself insufficient to account for the ^3He abundance in the air, although it may be adequate to provide much of the ^3He found in gas wells and in minerals. Another mechanism has been suggested by Libby (1946), namely the transformation of ^{14}N in the air by fast neutron bombardment from cosmic rays in the reactions $^{14}\text{N}(n, ^{12}\text{C})^3\text{H}$ and $^{14}\text{N}(n, 3\alpha)^3\text{H}$, after which the ^3H decays to ^3He . Libby estimated that although the reactions require high energy neutrons (see Cornog and Libby 1941) they would be sufficiently frequent to account for the ^3He content of the air.

The concept that cosmic rays provide the primary mechanism in the production of ^3He in the atmosphere and in the lithosphere is of interest, particularly if attention is paid to the occurrence of nuclear evaporation as is evidenced by cosmic ray 'stars', for it provides yet another mechanism to explain the occurrence of ^4He also. In the past it was supposed that ^4He was either of primordial origin or was the product of radio-active decay (Rodgers 1921). The known abundance of ^4He in radio-active minerals together with the apparent complete absence of ^3He strongly supports the second of these hypotheses as far as radio-active minerals are concerned. The occurrence of both ^4He and ^3He in non radio-active sources, however, provides evidence for the cosmic ray mechanism. Here the recent experimental work of Huntley (1948) is of interest. Huntley measured the frequency of occurrence of nuclear evaporation due to cosmic ray bombardment of nuclei located in the glass base of photographic plates, the evaporations being evidenced by the so-called 'stars'. At the location of the experiment on the summit of Mont aux Sources, Basutoland, the quantity of helium produced in glass by such evaporations would, in a suitable geological period, (10^8 to 10^9 years), be of the same order of magnitude as that found in non radioactive minerals of high ^4He content such as beryl, thus showing that the cosmic ray star mechanism can account at least partly, for the ^4He and presumably for the ^3He found in non radioactive matter.

Note added in proof.—Recently Pine and Morrison (*Bulletin of The American Physical Society*, **27**, 21 (Jan.) 1952) have made experiments which are in support of the thesis proposed earlier by Morrison and Beard (1949), namely that the occurrence of ^3He as well as ^4He in the lithosphere is due to radioactive processes only. Morrison and Beard supposed that ^3He is created in the lithosphere by the reactions $^6\text{Li} (n, \alpha) ^3\text{H} : ^3\text{H} (\beta^-) ^3\text{He}$, as suggested previously by Hill (1941), but that the neutron source is *not* of cosmic origin. They considered that in granitic rock, located at depths where cosmic ray effects would be negligible, neutrons would be available due to inclusions of radio-active material in the rock through reactions such as: $\text{U}, \text{Th}, \rightarrow \alpha$; $\text{Si}, \text{Al}, \text{etc.}, (\alpha, n)$. Pine and Morrison (1952) reported that their experiments using a simulated granite enriched in radioactive mineral showed that the neutron yield in such sources would be sufficient to account, via the $^6\text{Li} (n, \alpha) ^3\text{H}$ reaction, for the observed ratio of $^3\text{He}/^4\text{He}$, for example, in gas-well helium.

§ 2. ENRICHMENT AND PRODUCTION OF ^3He

Apart from methods dependent on the properties of solutions of ^3He in liquid ^4He , which will be described in detail in § 3 below, the enrichment of ^3He in ^4He has been carried out by thermal diffusion. The theory of the thermal diffusion process together with notes on the application of the process to the ^3He and ^4He problem has been given in detail by Jones and Furry (1946). Any description, however, of the process is beyond the scope of this paper, which will be confined here

to a brief mention of the experimental results obtained by thermal diffusion. Experimental work on a thermal diffusion column for ^3He enrichment was first briefly reported by McInteer, Aldrich and Nier (1947), and from this the thermal diffusion constant was measured. They calculated a relaxation time for their apparatus of the order of 10^4 years and consequently were only able initially to report the rate of concentration increase in the column for conditions of negligible 'draw-off' gas. Subsequently these authors reported (Fairbank, Reynolds, Lane, McInteer, Aldrich and Nier 1948) enrichments up to about 0.15% ^3He in ^4He for draw-off volumes of 100 c.c. (NTP) and they gave a detailed description of their apparatus with operating data (McInteer, Aldrich and Nier 1948). Their system consisted of three columns in series, the first two being concentric cylindrical type and the third being a hot wire type, the whole arrangement being similar in character to the design originally suggested by Jones and Furry (1946). Starting with well-helium ($^3\text{He}/^4\text{He}=1.4 \times 10^{-7}$) it was possible with the expenditure of 16.6 kw to produce 14 c.c. (NTP) of helium gas per day having a $^3\text{He}/^4\text{He}$ concentration of 0.21%. A schematic diagram showing the flow system for this thermal diffusion plant is given in fig. 1 and dimensions and operating data are given in table 3.

Table 3. Dimensions and Operating Data for Thermal Diffusion Plant, according to McInteer, Aldrich and Nier (1948)

Type	Section 1	Section 2	Section 3
	Concentric cylinder	Concentric cylinder	Hot wire
Length (cm)	350	350	254
<i>Hot wall</i>			
Material	steel	steel	platinum
Radius (cm)	3.02	1.75	0.018
Temperature °K	600	600	1100
Power (kw)	10	5	1.6
Voltage	220 a.c.	220 a.c.	130 d.c.
<i>Cold wall</i>			
Material	brass	brass	brass
Radius (cm)	3.65	2.38	0.466
Temperature °K	300	300	300

Operating pressure=7.8 Atmospheres.

Rollin and Hatton (1948) and Andrew and Smythe (1948) have subsequently reported successful enrichments by thermal diffusion methods for small quantities of gas up to concentrations of ^3He in ^4He of about 1%. No details of their apparatus have however been published.

Recently Schuette, Zucker and Watson (1950) have given details of a thermal diffusion plant, using concentric tube type and hot wire columns in series and have reported that concentrations of ${}^3\text{He}/{}^4\text{He}=0.05\%$ have been obtained from well-helium. They stress the fact that thermal diffusion columns of the concentric tube type could be greatly improved by making the central tube of high thermal conductivity material in order to avoid azimuthal temperature gradients which cause parasitic remixing of the gas.

Fig. 1

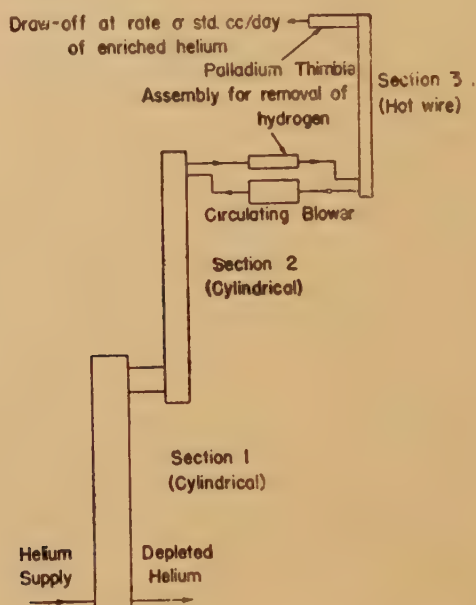


Diagram of thermal diffusion arrangement used by McInteer, Aldrich and Nier (1948) for the enrichment of ${}^3\text{He}$. Starting with 'well' helium they produced 14 c.c. (NTP) of gas per day with a ${}^3\text{He}$ concentration of 0.21% .

The production of *pure* ${}^3\text{He}$ was first reported by Sydoriak, Grilly and Hammel (1949), the isotope being obtained from tritium decay. A fuller description of the method of production has been given by Abraham, Osborne and Weinstock (1950) who stated that 'the helium three . . . was obtained from the decay of tritium gas which was prepared by neutron irradiation of lithium in a chain reacting pile. The tritium was initially separated from ${}^4\text{He}$, also formed in the nuclear reaction, by diffusion of the tritium through a heated palladium thimble. Subsequently the ${}^3\text{He}$ which had grown in was separated from the tritium by the same technique and was purified from traces of tritium by circulating the gas through a U-tube immersed in liquid helium. In this way 29.9 c.c. (NTP) of ${}^3\text{He}$ gas was obtained with a ${}^4\text{He}$ content, according to mass-spectrographic analysis, of $0.03 \pm 0.03\%$ '.

§ 3. EXPERIMENTALLY OBSERVED PROPERTIES OF SOLUTIONS OF ^3He IN ^4He

(a) Superfluidity and the λ -temperature

Pure liquid ^4He is unusual in having two distinct liquid phases, one of which is 'superfluid'. For reviews of earlier work on this phenomenon, see Keesom (1942), Burton, Grayson Smith and Wilhelm (1940). The effects of adding the rare isotope ^3He to liquid ^4He on the superfluid properties of the solution are therefore of more than passing interest.

The first experimental work on the superfluid properties of ^3He in solutions was by Daunt *et al.* (1947 a and 1947 b), who observed that the ^3He did *not* take part in the superfluid flow. They found that it was possible to filter out the ^4He from the dilute solutions by allowing the ^4He to flow in superfluid flow out of its container either through the mobile supra-surface film or through a narrow channel in the bulk liquid. The residue left in the container was thereby enriched in ^3He . A diagram of one apparatus used by Daunt *et al.* is given in fig. 2. The glass vessel *B* represents the main liquid helium bath maintained at constant temperature below the λ -temperature. The glass vessel *A*, situated in *B*, was partially filled with $^3\text{He}+^4\text{He}$ solution. Inside *A* a small Dewar vessel *D* was placed, so constructed that the top was closed off by an evacuated glass plug which was ground to fit the Dewar. On supplying heat electrically inside the Dewar *D*, liquid was transferred into it from the vessel *A* by superfluid flow through the supra-surface film, which could move easily through the narrow channel formed by the ground glass plug. Owing to the fact that the return flow of vapour through the plug was negligible, the liquid in *D* was completely isolated and the level could be increased above that in *A* by superfluid flow to any desired amount. It was found by mass spectrographic analysis of the helium taken from *D* that the liquid transferred by film flow contained no ^3He .

Further experiments by Daunt *et al.* (1947 b) showed that for superfluid flow taking place in the *bulk* of the solution below the λ -temperature the ^3He did not take part in the superflow. These results immediately suggested a new method of isotopic separation in the liquid phase by superfluid filtration.

Partial separations of the isotopes ^3He and ^4He , using techniques based on this non-superfluid property of ^3He in solution were made subsequently by Daunt *et al.*, Lane and co-workers (Lane *et al.* 1948, Reynolds *et al.* 1949), Rollin and Hatton (1948), Taconis (1950) and by Eselson and Lazarew (1950 a and 1950 b). A diagram of the first apparatus used by Lane and co-workers is given in fig. 3. A thick walled glass bulb *B* contained an electric heater, *H*. The bulb was connected via a 1.5 mm diameter glass capillary *C*, a 1.5 mm diameter Kovar tube *K* and thence via a 1.5 mm diameter capillary *T* to the outside of the cryostat. The whole was immersed in a bath of liquid helium contained in the Dewar *D* and maintained below the λ -temperature. The $^3\text{He}+^4\text{He}$ solution was

condensed in the bulb *B* until the levels were as indicated in fig. 3. After the heater *H* had been on for some minutes, a sample of gas was withdrawn via *T* and mass spectrographically analysed and found to be enriched in ^3He . The excess ^3He concentration produced in the sample in this way can be explained by the fact that the heater produces an

Fig. 2

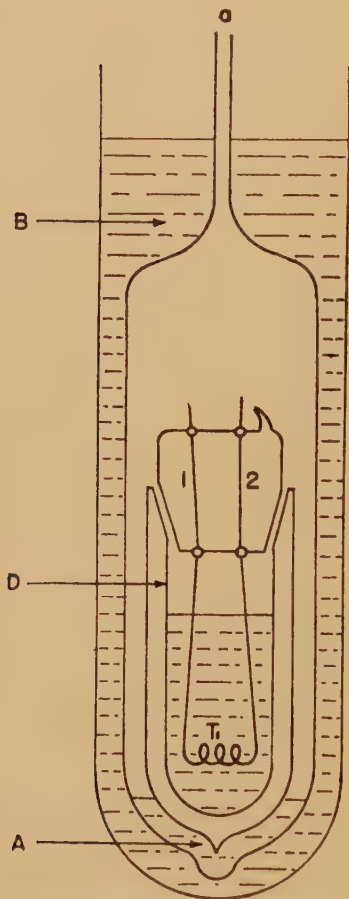


Diagram of apparatus used by Daunt *et al.* (1947 a) for investigating the flow properties of solutions of ^3He in liquid ^4He through supra-surface films.

Fig. 3

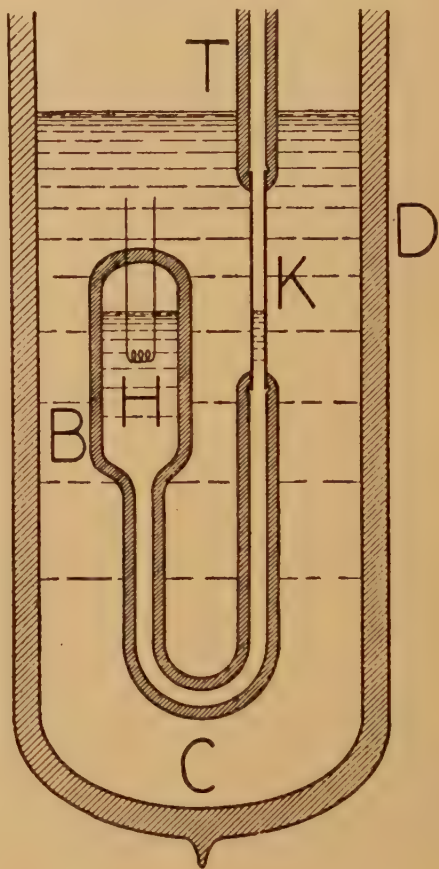


Diagram of apparatus used by Lane *et al.* (1948) for the enrichment of ^3He in mixtures of $^3\text{He} + ^4\text{He}$ by means of internal convection in the solution.

internal convection within the liquid, the superfluid part of the liquid flowing towards the source of heat and the 'normal' part away from it. If the ^3He does not partake in superfluid flow, then ^3He is carried by the normal flow only to regions far removed from the source of heat.

The processes of partial separation of the helium isotopes using the properties of the liquid phase as described above are powerful methods, and Taconis (1950) has reported their consistent use on a laboratory scale producing helium with a $\frac{1}{2}\%$ ^3He content starting from atmospheric helium for which the ^3He concentration is 1.2×10^{-6} . Owing to the expense involved in liquefaction, it is doubtful however whether these techniques will be widely used. An economic analysis of the relative costs of enriching ^3He in the liquid phase methods as compared with those involved in the chain reacting pile-method however has not yet been made.

The observed fact that in dilute solutions the ^3He does not take part in superfluid flow early led to the conclusion that the λ -temperature for ^4He would be a function of the ^3He concentration. The experiments which have been made to determine this function have, apart from their theoretical significance (see § 5 d), considerable importance for assessing the limitations of the liquid phase isotope separation process. Clearly, no further enrichment in ^3He content can be carried out using a method employing superflow at temperatures above the λ -temperature of the solution.

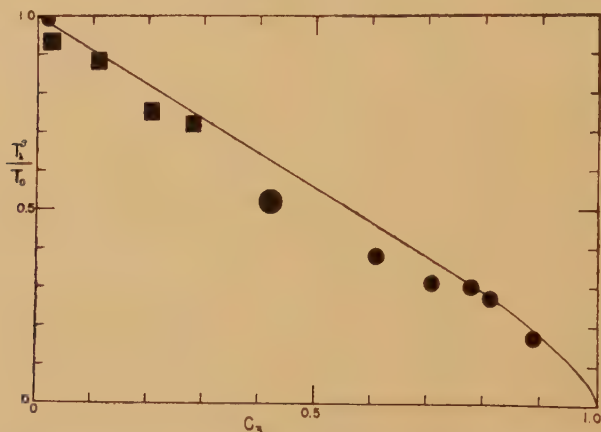
Measurements of the λ -temperatures of solutions of ^3He in liquid ^4He were first carried out by Abraham, Weinstock and Osborne (1949) using ^3He obtained from neutron initiated reactions in a chain reacting pile. In their experiments the $^3\text{He} + ^4\text{He}$ solution was condensed in a capillary tube which led to a very narrow channel ('superleak') formed around a platinum wire which had been sealed into the bore of the capillary (cf. Giauque, Stout and Barieau 1939). The rate of isothermal flow of helium through this superleak at temperatures between 1.0°K and 4.2°K was determined at successively lower temperatures by observing the rate of pressure rise in a large volume on the exit side of the leak. The temperature at which the measured flow rate began to rise sharply as the temperature was diminished marked the λ -temperature. Their results, obtained for solution concentrations between 2.4% and 28.2% , are given in table 4 and in fig. 4.

Table 4. λ -temperatures, T_λ^s , of Solutions of ^3He in liquid ^4He

Solution Concentration $C_L \%$	T_λ^s $^\circ\text{K}$	Author
1.5	2.15	Eelson and Lazarew (1950)
2.4	2.04 ± 0.05	Abraham <i>et al.</i> (1949)
10.7	1.92 ± 0.05	" " " "
20.3	1.63 ± 0.05	" " " "
28.2	1.56 ± 0.05	" " " "
42 ± 2	1.15 ± 0.05	Daunt and Heer (1950)
61 ± 2	0.82 ± 0.03	" " " "
71 ± 2	0.69 ± 0.03	" " " "
78 ± 2	0.64 ± 0.03	" " " "
81 ± 2	0.56 ± 0.03	" " " "
89 ± 2	0.38 ± 0.03	" " " "

Measurements using concentrations up to 89% have been made by Daunt and Heer (1950). In their apparatus the solution was condensed in a small reservoir thermally isolated in vacuo from the surrounding liquid helium bath but connected to the surroundings by a metal capillary. When the reservoir was cooled to a temperature below that of the surroundings, the rate of heat influx to it was strongly dependent on whether its temperature was above or below the λ -temperature of the solution. Below the λ -temperature of the solution the heat influx was very high, due to the motion of the supra-surface film up the inner wall of the capillary to the warmer end where it evaporated. (See Rollin 1936, Rollin and Simon 1939 and Daunt and Mendelssohn 1938 and 1939.) This upward flow of matter in the

Fig. 4



Plot of the experimentally observed values of the λ -temperatures, T_{λ}^s , of solutions of ^3He in liquid ^4He as a function of the solution concentration, C_3 . The λ -temperatures are plotted by the ratio of T_{λ}^s to the λ -temperature, T_0 , for pure liquid ^4He (2.18°K).

The circle at $C_3=1.5\%$ is the result of Eelson and Lazarew (1950), the squares show the results of Abraham *et al.* (1949) and the circles for $C_3>40\%$ are the results of Daunt and Heer (1950).

The full curve is the theoretical evaluation of the T_{λ}^s line made by Heer and Daunt (1951). (See § 5 (d).)

capillary was compensated by a downward flow in the vapour phase, bringing down to the lower temperature the high heat of condensation of the vapour. Above the λ -temperature this two-phase convection was absent and hence the observed heat influx to the reservoir much smaller. By observing the temperatures at which the heat influxes changed abruptly therefore the λ -temperatures for the different solutions were determined. To obtain temperatures below 1°K the reservoir was cooled by contact with a paramagnetic salt. The results are given in table 4 and in fig. 4. Further measurements have also been reported by Eelson and Lazarew (1950 b and 1950 c), who also used an

observation of the supra-surface film flow as the criterion for the existence of the λ -phenomenon, and their data are also included in table 4 and fig. 4.

The significance of these results will be discussed in detail in § 5. Two conclusions, however, might be added parenthetically here. First, the work of Daunt and Heer (1950) showed that the λ -temperature of the 89% solution was 0.38°K and that by extrapolation of the measured T_λ^s curve to 100% ^3He concentration it was concluded that pure ^3He could not be superfluid above 0.25°K and most probably not superfluid down to 0°K . Secondly, the curve for T_λ^s against ^3He concentration (fig. 4) reveals the highest ^3He enrichments that can be made at various temperatures by liquid phase superfluid separation. At 1.0°K , for example, which is the lowest temperature that can be conveniently maintained for long periods of time, solutions with a ^3He concentration greater than about 55% are no longer superfluid. 55% ^3He therefore marks the practical limit of enrichment using methods based on the superfluid filtration of ^4He from $^3\text{He} + ^4\text{He}$ solutions. Above these concentrations, rectification columns would be necessary for liquid phase separation, as has been pointed out by Taconis (1950). The use of a fractionating column has been reported by Eselson and Lazarew (1950 c).

(b) *Isotopic Osmosis*

During their experiments on the properties of ^3He in dilute solution with ^4He , Daunt *et al.* (1948) observed an osmotic effect between the two helium isotopes. They first demonstrated this effect using the apparatus diagrammatically illustrated in fig. 5, which consisted essentially of an inverted U-tube in one limb of which was placed a constriction, namely a ground glass plug, serving to prohibit the flow of vapour while allowing the free flow of liquid through the supra-surface film. The apparatus was maintained under isothermal conditions in a helium bath at temperatures below the λ -temperature. $^3\text{He} + ^4\text{He}$ solution (concentration $\approx 10^{-5}$) was condensed in the right hand limb, the left hand limb being initially empty. After some time the left hand limb would partially fill, ^4He *only* being transferred into it by supra-surface film flow through the constriction. Equilibrium would finally be established with the level in the right hand limb, containing $^3\text{He} + ^4\text{He}$, remaining *above* the level in the left hand limb which contained only ^4He . This difference in level was a measure of the osmotic pressure between the solution and pure liquid ^4He , the semi-permeable membrane being the supra-surface film. At the time these experiments were undertaken no data were available on the vapour pressures of pure liquid ^3He and consequently detailed quantitative data on osmotic pressures were not presented. This osmotic effect has subsequently been studied by Taconis, Beenakker and Dokoupil (1950), who found that the osmotic pressure, P , for solution concentrations C_L up to 2.2×10^{-3} is accurately given by the van't Hoff law, namely

$$P = \rho RT \cdot C_L. \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Their experiments were carried out using apparatus similar to that of Daunt *et al.* (1948) with one modification. With solution concentrations C_L as high as 10^{-3} the osmotic pressures, as measured against pure liquid ^4He , are of the order of one meter of liquid helium, an unmanagably large liquid level difference. Taconis, Beenakker and Dokoupil compensated this osmotic pressure by the 'fountain pressure' difference which was produced by heating the vessel containing the pure ^4He . By measuring

Fig. 5

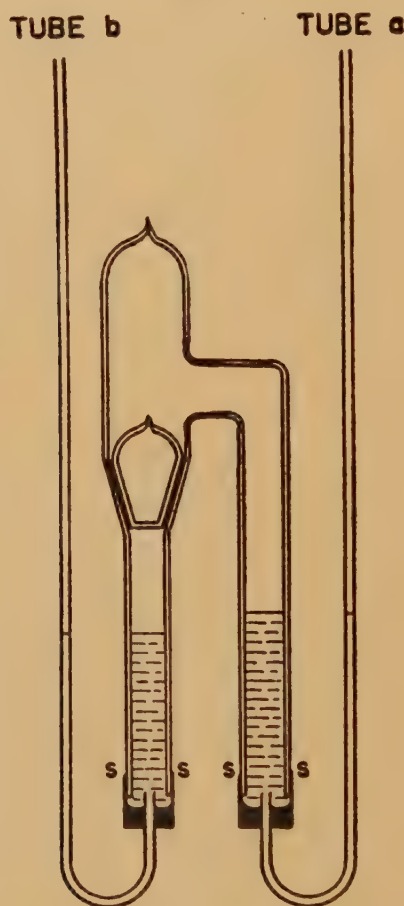


Diagram of apparatus used by Daunt *et al.* (1948) for the investigation of the osmotic pressures between solutions of ^3He in liquid ^4He and the pure liquid ^4He . The parts marked *s-s* represent copper glass seals. Tubes *a* and *b* lead to room temperature.

the temperature difference between the limb containing the pure ^4He and that containing the solution, the fountain pressure and hence the compensated osmotic pressure could be calculated using the well known formula for fountain pressure differences in liquid helium II. (See H. London 1939.)

solutions. The data reported by these authors however were not quantitative. Recent measurements by Daunt and Heer (1952), using a method which is described below, indicated also that C_v/C_L for solutions of about 1% ^3He content may be greater than the value calculable for perfect solutions. The uncertainty in their experimental values, which are shown in fig. 11, however, is unfortunately too great to allow a definite conclusion to be drawn. Theoretically exact data in this temperature range above T_λ^s would be of considerable importance (see § 5), and consequently further measurements would be of value.

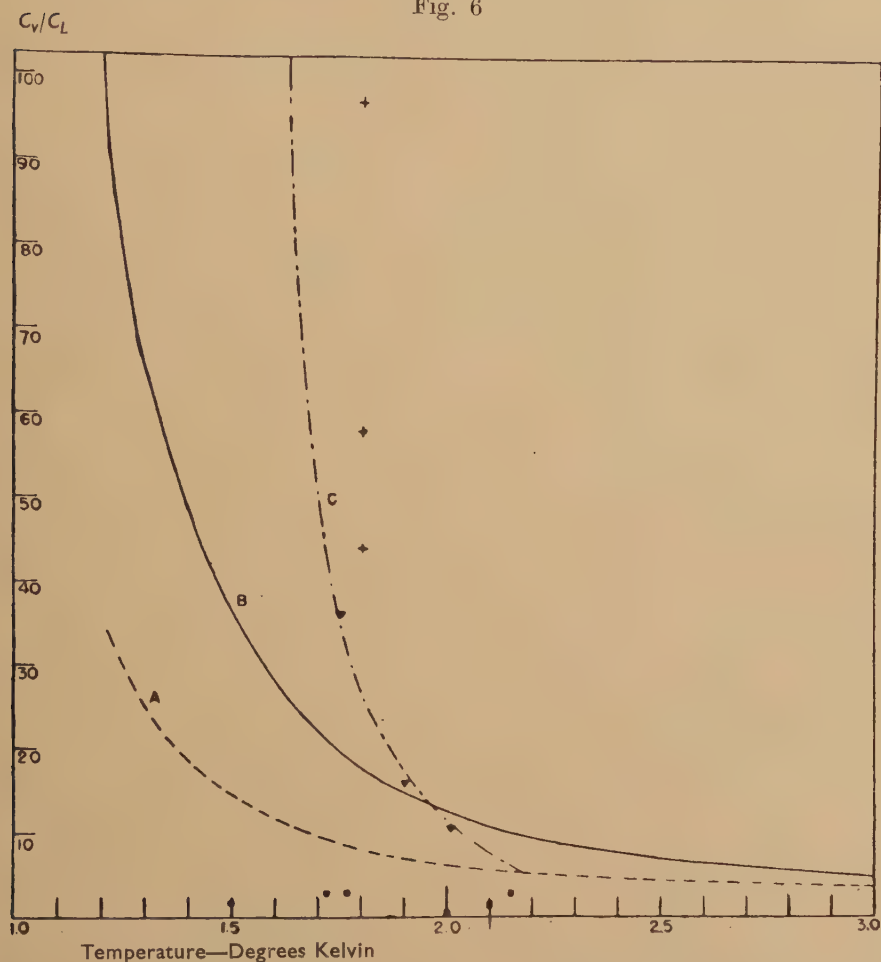
Measurements of the distribution coefficient *below* the λ -temperature show the greatest discrepancies between the results of various experiments, discrepancies which have been due mainly to a lack of homogeneity in the distribution of the ^3He throughout the volume of the liquid phase of the solution. This lack of homogeneity in the liquid phase has been due primarily (a) to the much larger heat influxes to the experimental arrangements at temperatures below the λ -temperature and (b) to the fact that ^3He in solution in liquid ^4He does not partake in superfluid flow. A careful weighting of the results of the measurements below the λ -temperature is therefore necessary.

The first results below T_λ^s reported by Daunt, Probst and Smith (1948) and by Fairbank, Lane *et al.* (1948) using very dilute solutions (concentrations of the unrefrigerated gas, $C_3, \approx 10^{-5}$) gave values for C_v/C_L all much *smaller* than are calculable from Raoult's law. Indeed the latter authors reported C_v/C_L to be zero for all temperatures below 1.8°K . Some of these results are included in fig. 6. These results can now be understood by consideration of the apparatus and method of measurement employed, as is diagrammatically shown in fig. 7. Here, a vessel containing a solution of ^3He and ^4He was immersed in a liquid helium bath below T_λ^s , and after time had been allowed for equilibrium to be established, a sample of vapour was withdrawn to room temperature and analysed mass spectrographically. Now below T_λ^s a supra-surface film is formed which moves up the inner wall of the tube *a*, partially evaporates higher in the tube and sends down a return vapour flow which brings in a heat influx, \dot{Q} (see fig. 7). This heat influx to the surface of the solution sets up an internal convection such that the superfluid constituent of the liquid helium moves to the surface (towards the source of heat) and such that the 'normal' constituent moves down. Since the ^3He does not partake in the superfluid flow, the result of this internal convection is to set up a marked concentration gradient within the solution with the surface depleted of ^3He . If, therefore, in such an arrangement the distribution coefficient is assayed by sampling and analysing the vapour, the result must give values of C_v/C_L that are too small, since at best the vapour sampled would have been in equilibrium with the solution at the surface.

Clearly to avoid the undesirable effects of internal convection the solution should be stirred, as was subsequently carried out by Taconis

et al. (1949 a and 1949 b). However, a way out of this difficulty without recourse to stirring was attempted with partial success by Lane and co-workers (1949). As is evident from fig. 7, the source of the heat influx which causes the unwanted internal convection in the solution is the filling and sampling tube, tube *a*. Lane and co-workers removed the

Fig. 6



Plot of the distribution coefficient, C_v/C_L , for solutions of ^3He in liquid ^4He against temperature for very dilute solutions ($C_L < 10^{-3}$).

The experimental observations are marked by the points, such that :

- represents work by Fairbank, Lane *et al.* (1948).
- represents work by Daunt, Probst and Smith (1948).
- ▼ represents work by Taconis *et al.* (1949 a, b).
- + represents work by Lane and co-workers (1949).

The theoretical evaluations of C_v/C_L for dilute solutions are shown by the curves. Curve *A* is computed from Raoult's law, curve *B* is computed from the theory of Heer and Daunt (1951), and curve *C* is computed using Taconis' hypothesis (Taconis *et al.* 1949 a, b). (For theoretical curves see § 5 (b).)

tube *a* and instead filled the solution reservoir with a tube from underneath (see fig. 8). The vapour above the solution was sampled by taking out the gas through a 'breakseal' arrangement, which closed off the top of the reservoir until the very moment of sampling. Their results (three points) with this arrangement are given in fig. 6, from which it will be seen that the experimental scatter is considerable (C_v/C_L varies by more than a factor 2 : 1 at $T=1.8^\circ\text{K}$). However, by introducing the

Fig. 7

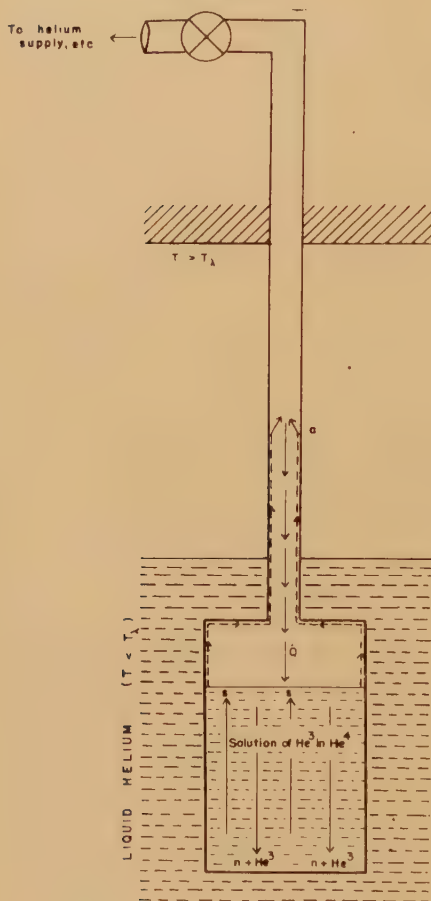
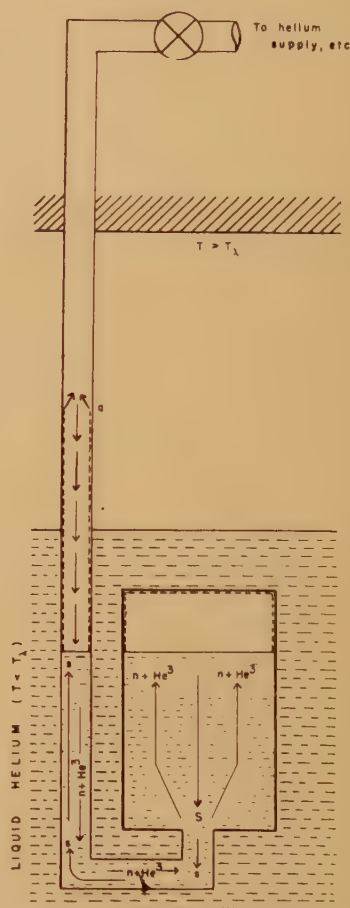


Fig. 8



filling tube at the bottom of the solution reservoir the direction of the heat influx is thereby reversed, and hence one would expect that the associated internal convection would tend to concentrate the ^3He at the surface of the solution, with the result that the measured C_v/C_L would be too high. The mechanism of this process is illustrated in fig. 8.

The apparatus in which the solution was stirred, used by Taconis *et al.* (1949 a and 1949 b) was identical in principle with the simple arrangement of fig. 7, the tube *a* leading not to a sampling bulb, however, but to a

differential oil manometer to measure the excess vapour pressure of the solution over that of the main liquid helium (^4He) bath. The concentration of ^3He in the vapour could then be calculated from the measured excess vapour pressure. Stirring was accomplished by allowing acoustical vibrations to occur in the gas column in the tube a , which were transmitted to the solution. The intensity of the acoustical vibrations were controlled by relative movement of another tube inside the tube a (see diagram in fig. 9). The results obtained for solution concentrations, C_L , of about 10^{-3} are given in fig. 6, and they indicate values of C_v/C_L much greater than those calculable from Raoult's law.

More recently measurements have been made of C_v/C_L for solutions with ^3He concentrations of about 1% by Daunt and Heer (1952) and by Sommers (1951 a and b). Daunt and Heer employed a technique similar to that of Taconis *et al.* (1949 b), except that no acoustical vibrations were permitted. The ^3He concentration in the vapour above the solution was calculated from the measured difference in vapour pressure, Δp , between the vessel containing the solution and an identical vessel containing pure liquid ^4He (see diagram in fig. 10). Stirring of the solution occurred automatically at the high concentrations used, since even a small excess concentration of ^3He at the bottom of the vessel would cause ebullition. The results are shown in table 5 and in fig. 11, from which it will be seen that the distribution coefficient, C_v/C_L , although higher in value than that calculable for perfect solutions, does not deviate from the values for perfect solutions by so great a factor as at lower concentrations (cf. figs. 6 and 11).

An extensive experimental investigation of ^3He in liquid ^4He solution has been made by Sommers (1951 a and b). He measured the equilibrium pressures of mixtures of known ^3He concentration both at the dew point and for the experimental reservoir full of the solution, covering the temperature range 1.2°K to 2.2°K and a wide range of ^3He concentrations. Full details of his results are yet to be published, however, some of the results* are shown in the figs. 19, 20, 21 and 22 which give the measured C_v/C_L for 1.00%, 5.00%, 10.00% solutions and as a function of C_L respectively. These results are of great value from a theoretical point of view (see § 5 (b)) and also should allow the presentation of detailed equilibrium diagrams, such as are necessary for assessing the efficiency of possible rectification columns for the separation of the isotopes.

(d) *Second Sound in Solutions of ^3He in Liquid ^4He . (Experimental)*

The velocity of second sound in liquid helium II (pure ^4He) has been measured extensively (see for example Peshkov 1944 and 1946, Lane, Fairbank and Fairbank 1947, Pellam 1949, Osborne 1951) and the results of such measurements have indicated that at the lower temperatures the

* I am greatly indebted to Dr. Sommers for permission to incorporate these results before his full paper on the subject has been published.

'normal' constituent of the liquid, although of very small abundance, plays a predominant role. It is to be expected therefore at lower temperatures additions of even small quantities of ^3He would profoundly affect the second sound velocity, since the motions of the ^3He are associated with the

Fig. 9

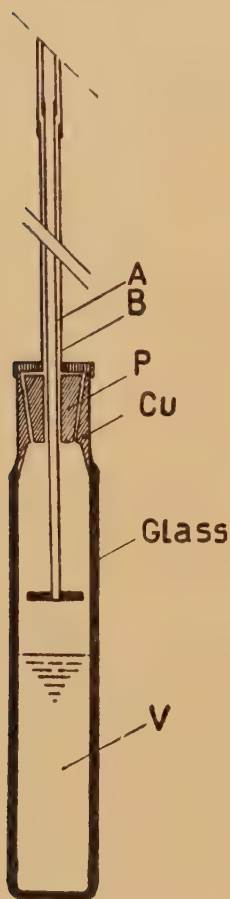


Diagram of apparatus used by Taconis *et al.* (1949 b) for investigation of the distribution coefficient, C_v/C_L , in solutions of ^3He in liquid ^4He . The vessel V , maintained at low temperatures, held the solution. The filling tube, Tube B , in this diagram is referred to in the text as 'tube a ' in order to compare with figs. 7 and 8.

Fig. 10

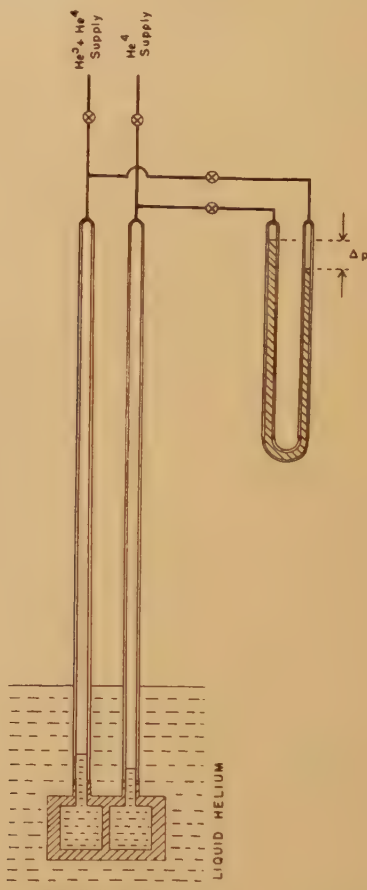
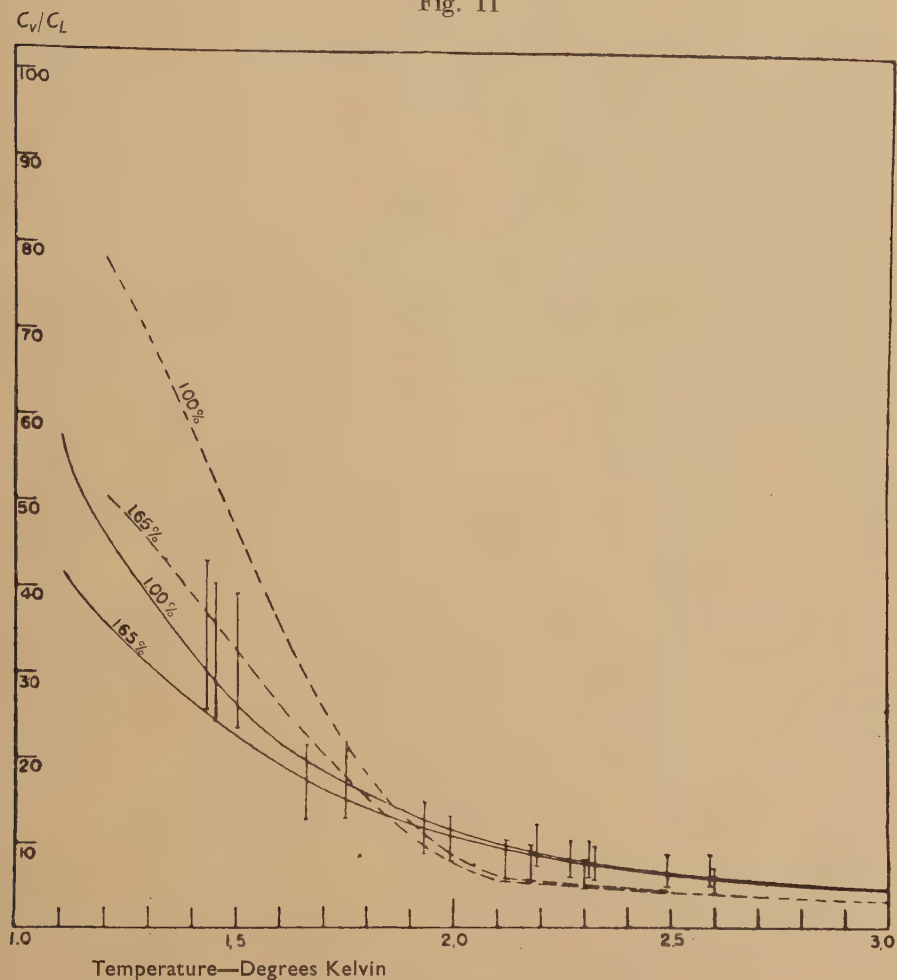


Diagram of apparatus used by Daunt and Heer (1952) for the measurement of the distribution coefficient, C_v/C_L , in solutions of ^3He in liquid ^4He .

normal constituent only. Detailed theoretical predictions of this effect have been made by Pomeranchuk (1949), as are discussed in § 5 (f) below.

Fig. 11



Plot of the distribution coefficient, C_v/C_L , for solutions of ^3He in liquid ^4He against temperature.

The vertical lines show the experimental results of Daunt and Heer (1952). The lengths of the vertical lines are due to doubt regarding the absolute value of the concentration of the unrefrigerated $^3\text{He}+^4\text{He}$ gas used. To interpret these lines, the upper ends refer to a 1.0% solution concentration of ^3He , whereas the lower ends of the vertical lines refer to 1.65% solution concentration. (See table 5 for numerical data.)

The curves are theoretical computations made by Daunt, Tseng and Heer (1952). The full curves are the computations for solutions with concentrations as marked using the theory of Heer and Daunt (1951), whereas the broken curves give the results of the computations using the theory of de Boer and Gorter (1950 a and b). (See § 5 (b) for theory.)

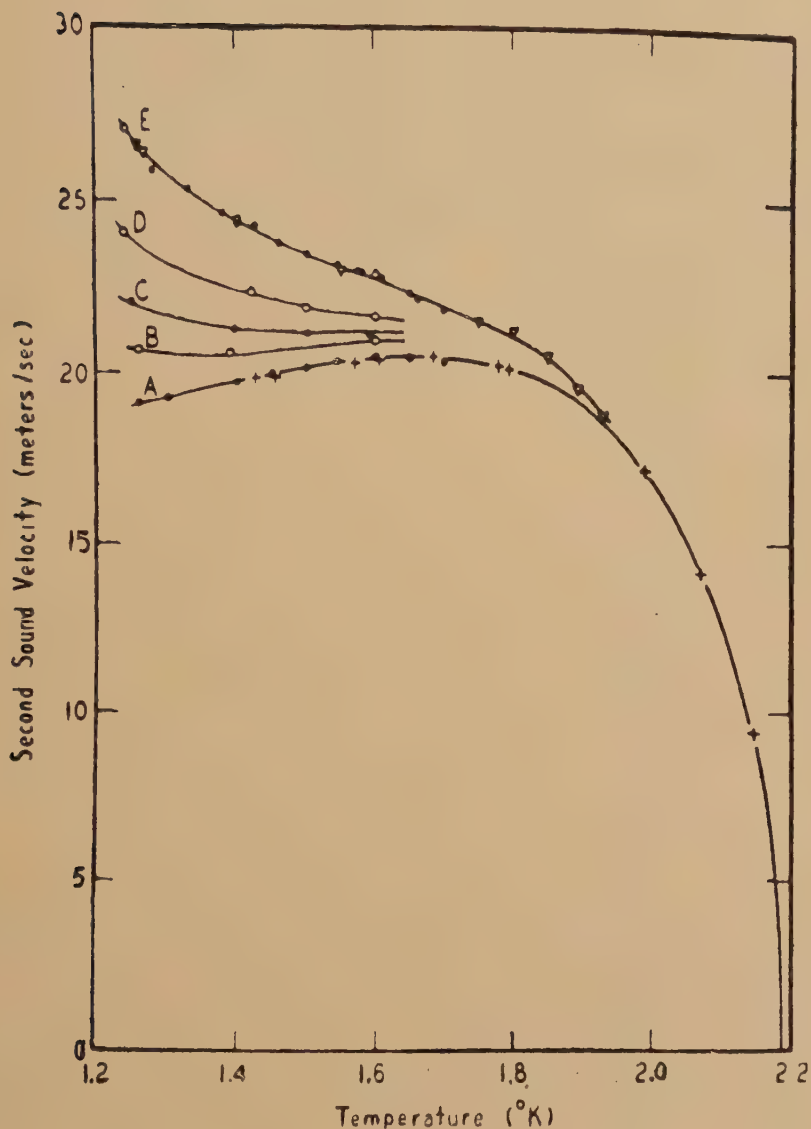
Experimental measurements of the velocity of second sound in solutions of ^3He in liquid ^4He have been made by Lynton and Fairbank (1950 a and 1950 b). The measurements were made in a small cylindrical reservoir immersed in a liquid helium bath, having at each end of the reservoir a carbon strip resistor. One resistor served to initiate thermal pulses in the solution, and the other served as a thermal detector. The time of flight of the pulses between the transmitter and detector was measured using standard radar techniques, and hence the second sound velocity determined. In their experiments care was taken to minimize the effects which would ordinarily accompany the heating of the solution at one end, which would result, as we have seen, in the setting up of unwanted concentration gradients within the volume of the solution, and in the measurement of inappropriate second sound velocities. The

Table 5. The Distribution Coefficient, C_v/C_L , for Dilute Solutions of ^3He in liquid ^4He , as measured by Daunt and Heer (1952), for C_L from 1.0 to 1.65%

Temperature °K	C_v/C_L ($C_L=1.0\%$)	C_v/C_L ($C_L=1.65\%$)
2.60	6.3	3.8
2.59	8.0	4.9
2.49	7.9	4.8
2.33	8.9	5.4
2.31	9.5	5.8
2.30	7.3	4.4
2.27	9.5	5.8
2.19	11.5	7.0
2.18	8.9	5.4
2.17	8.9	5.4
2.12	9.3	5.6
1.99	12.4	7.5
1.93	14.0	8.5
1.75	21.0	12.7
1.66	20.4	12.4
1.50	38.2	23.2
1.45	39.3	23.8
1.43	42.0	25.4

effects of the heat input were minimized by (a) pulsing the measuring current through the detector and (b) operating only with single pulses. The measurements were made using ^3He concentrations in the solution of 0.09% to 0.80%, which were known to an accuracy of 5%. The results obtained are shown in fig. 12, from which it will be seen that the second sound velocity increased markedly with increase of ^3He concentration, e.g. at 1.26° K the velocity with the 0.80% concentration was 26.52 m/s as compared with 19.08 m/s for pure ^4He . This behaviour of the second sound velocity is in general qualitative agreement with the predictions of Pomeranchuk (1949), and indicates the importance of even small additions of ^3He at the lower temperatures.

Fig. 12



Plot of the second sound velocity, u_2 , as a function of temperature for different concentrations of ^3He , as measured by Lynton and Fairbank (1950 b).

Curve *A* is for pure ^4He .

Curve *B* is for 0.09% ^3He .

Curve *C* is for 0.21% ^3He .

Curve *D* is for 0.41% ^3He .

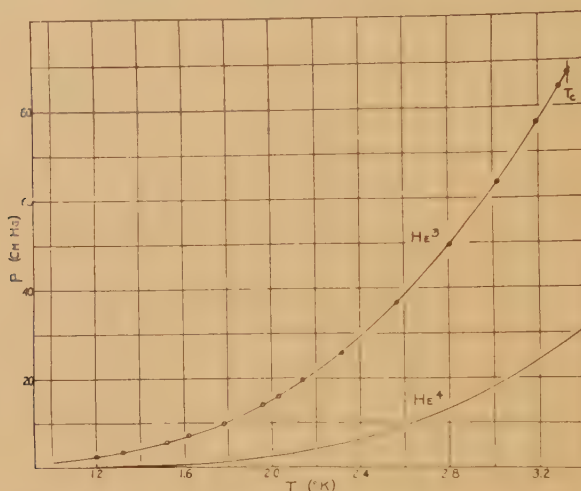
Curve *E* is for 0.80% ^3He .

§ 4. EXPERIMENTALLY OBSERVED PROPERTIES OF PURE LIQUID AND SOLID ^3He

(a) *Liquid ^3He*

Pure ^3He was first condensed and the vapour pressure of the condensed phase measured by Sydoriak, Grilly and Hammel (1949). They used pure ^3He prepared at Los Alamos Scientific Laboratory from the decay of tritium. The measurements were made by condensing the ^3He at the bottom of a steel capillary immersed in a liquid helium (^4He) bath and by observing the equilibrium pressure in the capillary at various temperatures. Condensation was assumed to have taken place when this pressure was independent of the external gas volume. They reported a boiling point of 3.20°K and a critical point of 3.34°K . Their vapour pressure data,

Fig. 13



Plot of the vapour pressure, P , of liquid ^3He and of liquid ^4He against temperature. The ^3He data are from the experiments of Sydoriak, Grilly and Hammel (1949).

together with the well known curve for pure liquid ^4He , are shown in fig. 13, in which it will be seen that the vapour pressure of the condensed ^3He is considerably higher than that of pure liquid ^4He .

Subsequent experiments by the same authors (Grilly, Hammel and Sydoriak 1949) using similar apparatus but with a glass capillary condensation tube showed that the ^3He condensed phase was liquid. The liquid ^3He was observed to be clear and colourless with a sharp meniscus. They observed that at one temperature (1.7°K) sudden reduction of the ^3He pressure caused a violent boiling similar to that observable in liquid helium I.

Subsequent measurements of the vapour pressure curve by Abraham, Osborne and Weinstock (1950) have been made, also using ^3He obtained

from tritium decay. They confirmed the previous evaluations of the boiling point and critical point and presented their data for the vapour pressures between 1.02°K and 3.35°K by the empirical formula :

$$\log_{10} p_{mm} = -\frac{0.97796}{T_K} + 2.5 \log_{10} T_K + 0.000302 T_K^3 + 1.91594 \dots \quad (3)$$

where T_K is the absolute temperature obtained by measurement of the liquid ^4He vapour pressure and by using the corrected 1949 ^4He temperature scale (van Dijk and Shoenberg 1949) as corrected by Kistemaker (1946). Since the temperature of the liquid ^4He bath was controlled in their experiments to only about 0.001°K , it would appear that the number of significant figures in the above equation for the ^3He vapour pressure is too large. Their experimental data are presented in table 6.

Table 6. Observed Vapour Pressures of Liquid ^3He from Abraham *et al.* (1950)

T_A $^\circ\text{K}$	T_K $^\circ\text{K}$	P (mm of Hg)
1.025	1.025	9.71
1.026	1.026	9.81
1.038	1.038	10.41
1.042	1.042	10.46
1.058	1.058	11.29
1.121	1.121	14.74
1.182	1.182	18.79
1.183	1.183	18.68
1.298	1.298	28.00
1.363	1.363	34.16
1.513	1.513	52.59
1.647	1.644	72.78
1.792	1.785	99.65
1.945	1.935	135.0
2.057	2.046	165.1
2.175	2.162	201.1
2.269	2.257	234.2
2.393	2.382	282.7
2.527	2.517	342.4
2.623	2.614	389.8
2.729	2.722	446.6
2.802	2.796	489.0
2.911	2.906	555.3
3.004	2.999	616.9
3.115	3.112	697.4
3.206	3.203	765.6
3.282	3.280	827.7
3.307	3.305	849.9
3.314	3.313	856.5
3.318	3.316	859.5
3.351	3.350	888.7

The temperature marked T_A (column 1 above) is obtained using the 1949 Scale of Temperature for the observed liquid ^4He vapour pressures (for a tabulation of the 1949 Scale see van Dijk and Shoenberg 1949). The temperature marked T_K is obtained using the correction proposed by Kistemaker (1946).

An indirect measurement of the liquid density of ^3He as a function of temperature was made by Grilly, Hammel and Sydoriak (1949). The procedure was as follows: ^3He was liquefied in their glass capillary condensation tube to a height of several millimeters (the inside diameter of the tube was 1.656 mm), then most of the liquid was evaporated by increasing the room temperature gas volume by a measured amount, ΔV_r . Since the evaporated liquid was replaced by vapour at the same temperature, the data gave the difference between the liquid and vapour densities:

$$\rho_L - \rho_v = \frac{3.02 \times 273}{22400 \times 760} \times \frac{p \cdot \Delta V_r}{T_r \cdot \Delta V_L}, \quad . . . \quad (4)$$

where p is the vapour pressure at the temperature of the measurement in mm of Hg, T_r the room temperature and ΔV_L the liquid volume change due to the change in liquid height. The results are given in table 7. In

Table 7. Differences between Liquid and Vapour Densities of ^3He , $(\rho_L - \rho_v)$ (Observed), from Grilly, Hammel and Sydoriak (1949)

T °K	$(\rho_L - \rho_v)$ g/c.c.
1.27	0.0783 ± 0.00016
1.73	0.0781 ± 0.00023
2.26	0.0698 ± 0.0017
2.52	0.0661 ± 0.0016
2.79	0.0542 ± 0.0027

Table 8. Corrected Liquid Densities of ^3He , ρ_L , (Calculated), from Grilly, Hammel and Sydoriak (1949)

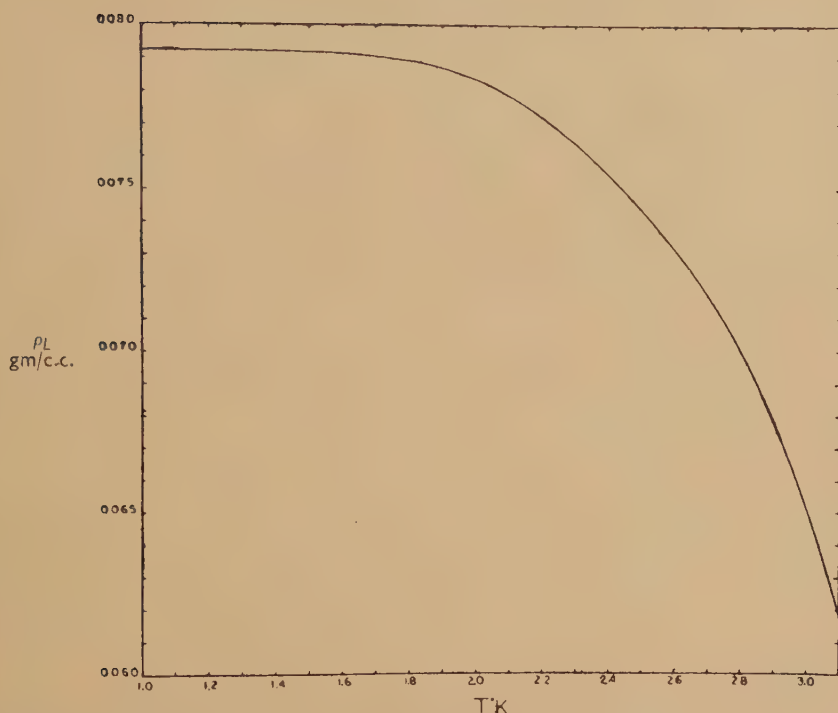
T °K	ρ_L g/c.c.
1.0	0.0792
1.5	0.0792
2.0	0.0784
2.5	0.0744
2.8	0.0700
3.1	0.0618

order to calculate the liquid density, ρ_L , the authors assumed the validity of the Law of Rectilinear Diameters with a value of the critical density 0.0420 g/c.c. These assumptions may prove to be somewhat in error, but the effect of such errors on the corrected liquid densities would be small (less than 3% at 2.5° K and still smaller at lower temperatures). On the other hand the vapour densities calculated in this way may be subject to considerable error. The corrected smoothed liquid densities calculated in this way are given in table 8 and are shown graphically in fig. 14.

The latent heat of evaporation of liquid ^3He has been calculated by Abraham, Osborne and Weinstock (1950) using the Clausius-Clapeyron equation. In this equation they used the corrected liquid densities given above (see table 8) and for dp/dT the vapour pressure formula given in eqn. (3). The vapour density they calculated from the equation of state:

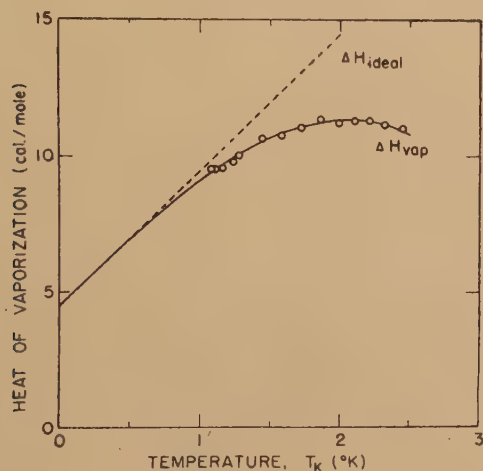
$$pV = RT[1 + B(T)/V] \quad \quad (5)$$

Fig. 14



Plot of the density of liquid ^3He against temperature, taken from the work of Grilly, Hammel and Sydoriak (1949).

Fig. 15



Plot of the *calculated* latent heat of evaporation, ΔH , of liquid ^3He , as computed by Abraham, Osborne and Weinstock (1950). The values ΔH_{vap} were obtained from the vapour pressure curve measurements. ΔH_{ideal} gives the slope of the curve at the absolute zero.

using the value of the second Virial coefficient, B , as calculated by van Kranendonk, Compaan and de Boer (1949). (See also de Boer and Kranendonk 1950.) Whereas the results do not have the certainty of direct experimental observation, they are of value as being a useful first approximation. They are shown in fig. 15.

The only measurement on liquid ^3He , apart from those on the vapour pressures and densities differences mentioned above, has been a qualitative measurement of the flow properties carried out by Osborne, Weinstock and Abraham (1949). This measurement was of importance for it established for the first time that pure liquid ^3He was not superfluid, at least down to 1.05°K . The later measurements of Daunt and Heer (1950) extended the range of the validity of this conclusion down to 0.25°K .

The apparatus used was the same as that employed by the same authors (Abraham, Weinstock and Osborne 1949) in measuring the λ -temperatures of solutions of $^3\text{He} + ^4\text{He}$ as described above in § 3 (a). Here the pure liquid ^3He was condensed in a capillary tube which led via a very narrow channel ('superleak') to a larger, initially empty, volume in which the pressure could be measured. The measurement consisted in observing the isothermal rate of pressure increase in the large volume on the exit side of the leak at various temperatures. The results are shown in fig. 16, which shows the results obtained with the same equipment both for pure liquid ^3He and for pure liquid ^4He . For pure liquid ^4He it will be seen that the rate of mass flow through the superleak increased very markedly at 2.18°K , i.e. at the λ -temperature, as would be expected. For pure liquid ^3He no such marked rise in the mass flow took place at any temperature employed, and consequently it was deduced that at least down to 1.05°K liquid ^3He is not superfluid. The observed decrease in the rate of mass flow as the temperature was decreased merely reflects the fact that the pressure head across the superleak was the vapour pressure of the liquid. Using the same apparatus, Weinstock, Osborne and Abraham (1949) were able to make a preliminary determination of the viscosity of liquid ^3He . Interpretation of the results was difficult, since within the 'leak' both the liquid and gaseous phases were present. However, by measuring the viscosity of the ^3He gas separately, these authors computed from their results that the viscosity of ^3He in the liquid phase increased from 22.0 micropoise at 2.79°K to 30.4 micropoise at 1.04°K .

(b) *Solid ^3He*

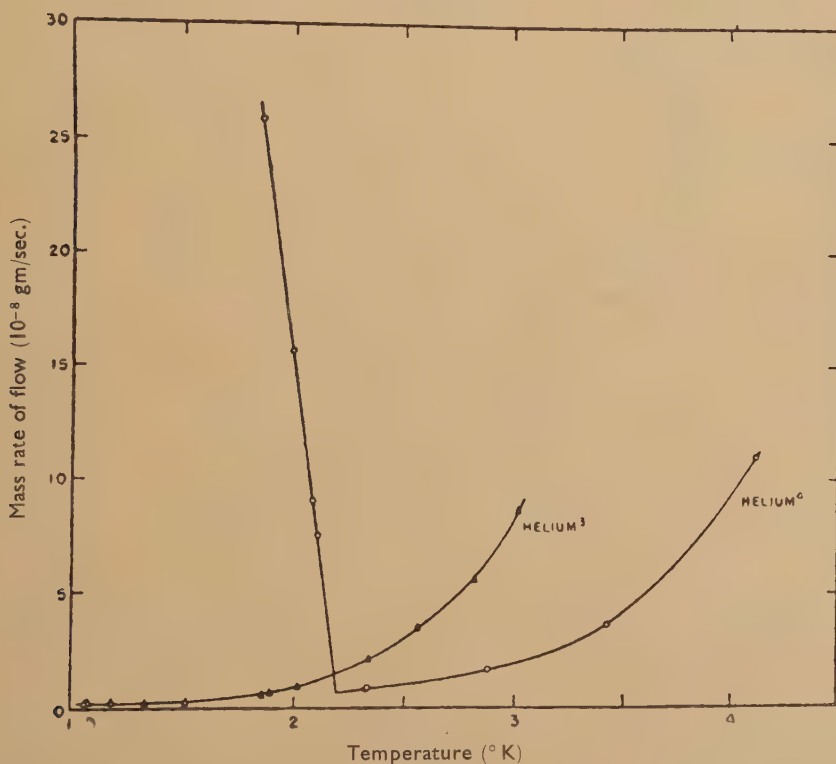
The melting curve for solid ^3He has been investigated by Osborne, Abraham and Weinstock (1951) in the temperature range 1°K to 1.5°K by the 'blocked capillary' method as has been used for solid ^4He by Keesom (1926) and extensively by Simon and co-workers (1929 and 1950). A diagram of the apparatus used in these measurements is given in fig. 17. The system was evacuated and then filled with 190 c.c. (NTP) of pure ^3He through the valves A and J . The gas was compressed by letting mercury into the volume H and the two gauges B and G would read the same

pressure until the capillary, D , maintained at the low temperature, got blocked with solid ^3He . In this way the melting pressure could be detected at various bath temperatures. The results are shown in fig. 18 and have been expressed by the formula

$$p_{\text{atmos}} = 27.0 + 13.0 T^2 \quad (6)$$

for the temperature range 1.02°K to 1.51°K . It is to be noticed that, as with ^4He , the melting pressure at the absolute zero of temperature is most probably positive, indicating that ^3He would not have a triple point but would remain liquid under its saturated vapour pressure down to 0°K .

Fig. 16



Plot of results of flow experiments for liquid flow through a very narrow channel for pure liquid ^3He and pure liquid ^4He by Osborne, Weinstock and Abraham (1949). The onset of superfluid flow in pure liquid ^4He below the λ -temperature of 2.18°K is shown in the diagram by the marked increase in the mass rate of flow through the narrow channel.

These authors (Abraham, Osborne and Weinstock 1951) have extended their measurements of the melting curve of ^3He down to 0.16°K , using the same blocked capillary technique and employing a paramagnetic salt to obtain the temperatures below 1°K . From 0.5°K upwards the

results confirm eqn. (6) and are shown in fig. 18. Below 0.5°K the experimental results appear to indicate an almost temperature independent melting pressure of 29.3 atmospheres (see fig. 18). This unexpected behaviour below 0.5°K may be due to poor thermal equilibrium in the experimental arrangement used, and comment is withheld pending further information.

§5. THEORIES OF SOLUTIONS OF ^3He IN ^4He

(a) *Superfluidity*

Much of the theoretical interest in solutions of ^3He in liquid ^4He is due to the information gained thereby on the properties of the pure solvent, especially below the λ -temperature of ^4He . The properties of

Fig. 17

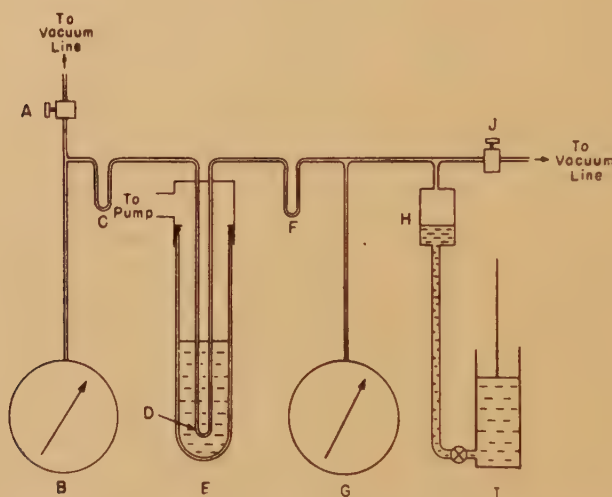
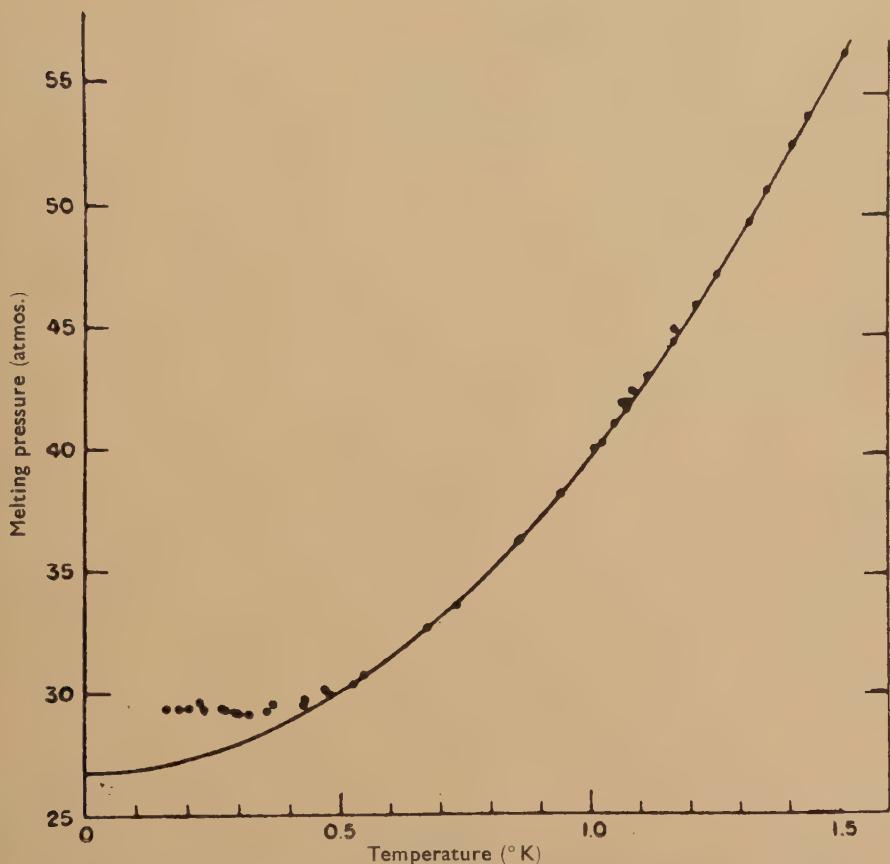


Diagram of the apparatus used by Osborne, Abraham and Weinstock (1951) for measurement of the melting pressures of solid ^3He by the blocked capillary method. ^3He was solidified in the capillary D under pressure.

pure liquid ^4He , as helium II, are unusual and are currently explained phenomenologically by a two-fluid theory. The two-fluid theory supposes that helium II is a mixture in configurational space of a 'superfluid' constituent, which can move (at least for low velocities) without friction, and a 'normal' constituent which shows viscous losses. The first theoretical ideas proposing a two-fluid model were put forward by F. London (1938 a and 1938 b), who suggested that the transformation of helium I into helium II was analogous to the degeneration which can occur at low temperatures in a perfect Bose-Einstein gas. That fraction of the gas, which in such a degeneration was grouped in the lowest energy state, was identified by London with the superfluid constituent; whereas the 'uncondensed' remainder

were associated with the 'normal' constituent of helium II. One essential feature of the theory lay in the fact that such a grouping or 'condensation' of atoms into a zero energy state would occur only for systems obeying Bose-Einstein statistics, and hence the occurrence of superfluidity would be governed primarily by the statistics. An alternative basis for a two-fluid model was proposed by Landau (1941 and 1944), who considered the possibility of the simultaneous occurrence

Fig. 18



Plot of the melting pressure of solid ^3He against temperature, as measured by Osborne, Abraham and Weinstock (1951). (See also Abraham *et al.* 1951.)

of potential and viscous motions in the liquid, such that the mass associated with the potential motion was identifiable with the 'superfluid' constituent of helium II. On this basis the occurrence of superfluidity appeared uninfluenced by the statistics.

It was suggested by Pollard and Davidson (1942), by Franck (1946) and by Onsager (unpublished, but see Lane *et al.* 1948) that if the London theory were correct the criterion for superfluid flow of the helium isotopes in solution would be whether they obeyed the Bose-Einstein statistics,

^3He , therefore, they suggested, would not be expected to show superfluid properties in solution with ^4He , since the ^3He obeys Fermi-Dirac statistics. The experimental work by Daunt *et al.* (1947 a and 1947 b), outlined in §3, showed that indeed ^3He in solution in ^4He did not partake in superfluid flow. This important result, although of fundamental value in interpreting the behaviour of solutions of ^3He in ^4He , did not, however, provide the critical test of the London theory, as had been suggested. According to Landau and Pomeranchuk (1948) any impurity particle in helium II would not partake in superfluid flow, and for extreme dilution it was possible to regard the ^3He atoms as impurities. Moreover in a subsequent development of London's theory made by Heer and Daunt (1951), it was found that many of the properties of the solutions could be explained by assuming that the ^3He and ^4He formed statistically independent assemblies and hence that a diluent, such as the ^3He , in low concentration must be characterized only by Maxwell-Boltzmann statistics. These considerations led to the conclusion that a solution of two Bose-Einstein liquids (e.g. ^6He and ^4He) should show two λ -transitions (if each separately in the pure phase showed a λ -transition), each λ -temperature being determined by the number density of each component considered separately. For *dilute* solutions therefore the superflow of the diluent, if at all possible, would not be evident until extremely low temperatures were attained, as had been pointed out by Daunt *et al.* (1947 a).

On the other hand the experiments of Osborne *et al.* (1949) and of Daunt and Heer (1950) established that *pure* liquid ^3He did not show superfluidity, even down to 0.25°K and established therefore the fundamental significance of the statistics in the theory of superfluids, as originally postulated by F. London, since the ^3He in the pure form must be considered as a Fermi-Dirac statistical assembly. A short note emphasizing this conclusion has been published by F. London (1949).

(b) *The Distribution Coefficient*

From their experimental results Taconis *et al.* (1949 a and 1949 b) deduced that the deviations of the measured values of the distribution coefficient for very dilute solutions of ^3He in ^4He from Raoult's law (see eqn. 2) could be explained by assuming (a) that the solutions were perfect, i.e. independence of the energy of one atom of ^3He or ^4He of the concentration, and (b) that liquid helium is a two-fluid system with the ^3He soluble in the 'normal' constituent only. For very dilute solutions the above assumptions lead to the following formulation for C_v/C_L :

$$C_v/C_L = \rho/\rho_n \cdot p_3^0/p_4^0 \quad \dots \quad (7)$$

where ρ and ρ_n are the total density of liquid ^4He and the density of the 'normal' constituent of helium II respectively. By using the approximation proposed by Tisza (1947) (an approximation valid at least in the temperature region concerned, 1.6°K to 2.18°K) which puts $\rho_n/\rho = S/S_\lambda$, where S and S_λ are the entropies of the liquid ^4He at the temperature of interest and at the λ -temperature respectively and by using the known

values for the entropy (see Band and Meyer 1948 and Gorter, Kasteleijn and Mellink 1950 for entropy tabulations) the value of C_v/C_L according to eqn. (7) can be calculated and the result is shown in fig. 6, by the broken curve 'C'. It will be seen in fig. 6 that the results of Taconis *et al.* (three points) are in substantial agreement with eqn. (7). It should be pointed out also that, if the assumption (a) above is continued to be assumed valid above the λ -temperature, there should be no difference between eqns. (7) and (2), since above the λ -temperature $\rho_n/\rho=1$. This means therefore that, according to Taconis, Raoult's law should be at least approximately valid above the λ -temperature.

A more general derivation for the value of the distribution coefficient, C_v/C_L , even for strong solutions of ^3He in ^4He has been given by de Boer and Gorter (1950 a and 1950 b), starting from the basic hypothesis of Taconis, namely that the ^3He is soluble only in the normal constituent of helium II. Regarding the solution as being classically perfect, de Boer and Gorter write down the total Gibbs function, G , as

$$G = (N_4/N) G_4 + (N_3/N) G_3 + kT [N_4^n \ln N_4^n + N_3 \ln N_3 - (N_4^n + N_3) \ln (N_4^n + N_3)]. \quad (8)$$

This is identical with the usual Gibbs function for mixtures except in the mixing term N_4^n is used instead of N_4 , where N_4^n represents the number of ^4He atoms in the 'normal' fraction of the helium II. By so changing the usual mixing term, de Boer and Gorter take account of Taconis' hypothesis. It should be noted here that the form given above for the mixing term in the Gibbs function requires the usual assumption that the difference between the arithmetic mean and the geometric mean of the molar volumes is small. This expression for G can be rewritten, using the symbols X for the liquid concentration (C_L) and X_e the effective ^3He concentration in the 'normal' constituent, where

$$\left. \begin{aligned} X &= C_L = N_3 / (N_3 + N_4), \\ X_e &= N_3 / (N_3 + N_4^n) = X / [X + (1-X)x], \\ \text{and where } x &= N_4^n / N_4 = \rho_n / \rho. \end{aligned} \right\} \quad (9)$$

Thus G can be written :

$$G = (1-X)G_4 + XG_3 + RT(X/X_e)[X_e \ln X_e + (1-X_e) \ln (1-X_e)]. \quad (10)$$

Now following previous work of Gorter (1949), the equilibrium value of G is obtained by minimizing with respect to the number of 'normal' atoms, N_4^n . This gives the following implicit expression for x :

$$(\partial G_4 / \partial x)_T + RT \ln (1-X_e) = 0. \quad (11)$$

To obtain the vapour pressures of the solutions and hence the value of C_v/C_L , de Boer and Gorter first calculated the partial potentials μ_3^L and μ_4^L in the liquid phase in the usual way from the Gibbs function, G , and the partial potentials μ_3^v and μ_4^v in the vapour phase by assuming the vapour to be a perfect gas. Then the condition for

equilibrium between liquid and vapour was applied, namely that the partial potential in the vapour phase is equal for each component whether in solution or in the pure phase to the partial potential in the liquid phase, i.e. that :

$$\left. \begin{aligned} \mu_3^L - \mu_3^{0L} &= \mu_3^v - \mu_3^{0v} = kT \ln (p_3/p_3^0), \\ \mu_4^L - \mu_4^{0L} &= \mu_4^v - \mu_4^{0v} = kT \ln (p_4/p_4^0), \end{aligned} \right\} \quad \dots \dots \dots (12)$$

where the superscript 0 refers to the pure phase and where p_3 and p_4 are the partial vapour pressures and p_3^0 and p_4^0 the full vapour pressures of pure liquid ^3He and ^4He respectively. The results for C_v/C_L are :

Above the λ -temperature, T_λ^0 , of the solution

$$\frac{C_v}{C_L} = \frac{p_3^0(X_e/X)}{p_3^0 X_e + p_4^0(1-X_e)^{x_0}}, \quad \dots \dots \dots (13a)$$

and below the λ -temperature, T_λ^0 , of the solution :

$$\frac{C_v}{C_L} = \frac{p_3^0(X_e/X)}{p_3^0 X_e + p_4^0(1-X_e)^x \exp \{ [G_4(T, x) - G_4(T, x_0)]/RT \}}, \quad (13b)$$

where x_0 is the value of x at T_λ^0 .

For small concentrations of ^3He , i.e. for $X \ll 1$, (13b) reduces to the equation previously given by Taconis *et al.*, i.e. to eqn. (7).

In making numerical evaluations of C_v/C_L from (13a) and (13b) some assumption must be made regarding the Gibbs function, G_4 , for pure liquid helium four as a function of T and x . For this de Boer and Gorter used a two-fluid model which had previously been proposed by Gorter (1949). In essentials this phenomenological model was closely analogous to a two-fluid model for superconductivity put forward by Gorter and Casimir (1934). The model assumed that the Gibbs function could be written as the sum of two terms, one for the superfluid and the other for the 'normal' constituent, which was separated from the superfluid by an energy gap, viz. :

$$G_4(T, x) = -E_0(1-x^{7/6}) - xS_\lambda T. \quad \dots \dots \dots (14)$$

This expression was chosen so as to conform to the approximate representation of experimental data given by Tisza (1947), which stated that in the temperature range 1.2° K to 2.18° K

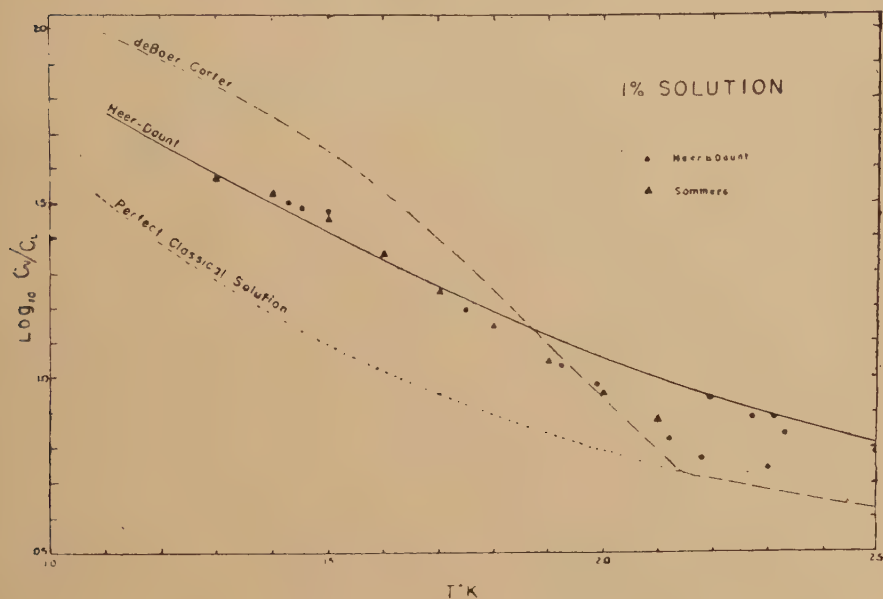
$$x = \frac{\rho_n}{\rho} \approx \frac{S}{S_\lambda} \approx \left(\frac{T}{2.18} \right)^6. \quad \dots \dots \dots (15)$$

The curious index of 7/6 in the power of x in the first term on the right-hand side of eqn. (14) was arrived at so as to make $S_4 = -(\delta G_4/\delta T)$ proportional to T^6 , as is approximately experimentally observed in the temperature range 1.2° K to 2.18° K. S_λ was taken equal to 0.8 R .

Although the expression for G_4 given in (14) is arbitrary (a fuller discussion of this is given in § 5(d)), it can be used for calculating C_v/C_L from eqns. (13a) and (13b), as has been done by Daunt, Tseng and

Heer (1952). The results of these computations are shown by the broken curves in fig. 11 (for $C_L=1.00$ and 1.65%), in fig. 19 (for $C_L=1.00\%$), in fig. 20 (for $C_L=5.00\%$) and in fig. 21 (for $C_L=10.00\%$). Also in these figures curves are included showing the evaluation of C_v/C_L for perfect classical solutions and according to the theory of Heer and Daunt (1951). One interesting feature of these results which is clearly evident for the 5.00 and 10.00% solutions is that for the temperature range between the λ -temperature of the solution, T_λ^s , and 2.18°K (the λ -temperature for the pure solvent), C_v/C_L according to the theory of de Boer and Gorter is *smaller* than that calculable from the laws for

Fig. 19



Plot of the distribution coefficient, C_v/C_L , for a 1.0% solution of ^3He in liquid ^4He against temperature. The three curves are the results of computations by Daunt, Tseng and Heer (1952) using the theories (as marked in the diagram) of Perfect Classical Solutions, de Boer and Gorter (1950 a and b) and of Heer and Daunt (1951).

Experimental measurements are shown by the points.

● represents data of Daunt and Heer (1952).

▼ represents data of Sommers (1951 a and b and private communication).

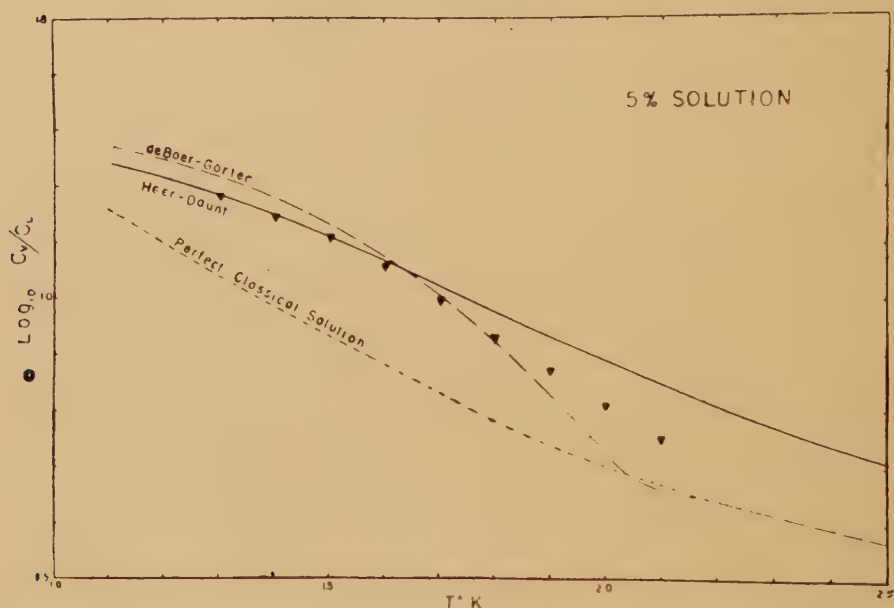
The writer is indebted to Dr. Sommers for permission to use his results here before full publication.

perfect classical solutions. This is due, as de Boer and Gorter (1950 b) have pointed out, to the fact that in solutions above T_λ^s all ^4He atoms are in the normal state, whereas for pure ^4He at the same temperature part of the atoms would be in the superfluid state,

As might be expected at any one temperature there is a considerable variation of C_v/C_L with the solution concentration C_L , and as C_L is increased there is less and less difference between the values of C_v/C_L on de Boer and Gorter's theory and for perfect classical solutions. The variation of C_v/C_L , as computed by Daunt, Tseng and Heer (1952), with C_L for two isotherms at 1.4° K and at 2.15° K is shown in fig. 22.

A different method of approach, originally proposed by de Boer (1949) and included in the considerations of de Boer and Gorter (1950 a and 1950 b), considered that the fraction x of 'normal' fluid present at any temperature was independent of the addition of ^3He to the solution, i.e. that the internal properties of each component are not changed in

Fig. 20



Plot of the distribution coefficient, C_v/C_L , for a 5.0% solution of ^3He in liquid ^4He against temperature. The three curves are the results of computations by Daunt, Tseng and Heer (1952) using the theories (as marked in the diagram) for Perfect Classical Solutions, of de Boer and Gorter (1950 a and b) and of Heer and Daunt (1951).

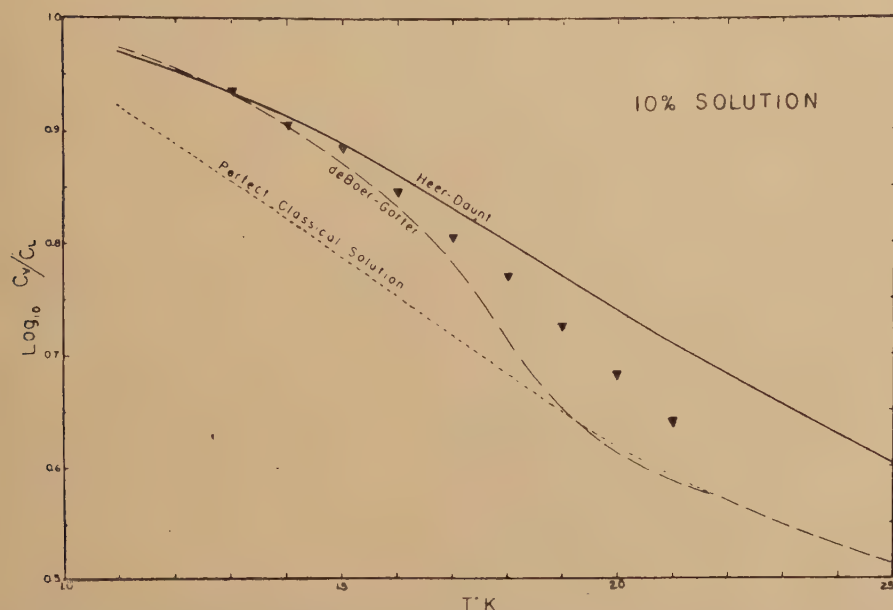
Experimental measurements by Sommers (1951 a and b and private communication) are shown by the points.

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the mixing process. With this approach the development of the thermodynamics based on eqn. (10) for the Gibbs function of the solution lead to the conclusion that for all concentrations X , other than $X=0$, the λ -transition would be of first order and that on cooling a given solution a separation of phases into helium I and helium II would occur,

The possibility of the phase separation has been studied experimentally by Weinstock, Osborne and Abraham (1950) in the following way. By the phase rule if two liquid phases and a vapour phase are present in equilibrium in a two component system, such as $^3\text{He} + ^4\text{He}$, there is only one degree of freedom, and hence the vapour pressure must be a function of temperature alone and independent of the concentration. Weinstock *et al.* therefore measured the vapour pressure of a 20.3 and a 25.5% solution of ^3He in liquid ^4He as a function of temperature down to a temperature of 1.04°K , which would be a much lower temperature than those calculated by de Boer (1949) for the initiation of phase separation in such solutions. The experiments showed that over the whole range of temperature measured (3.2°K to 1.04°K) the vapour pressures of the two solutions at any one temperature were different from another.

Fig. 21



Plot of the distribution coefficient, C_v/C_L , for a 10.0% solution of ^3He in liquid ^4He against temperature. The three curves are the results of computations by Daunt, Tseng and Heer (1952) using the theories (as marked in the diagram) of Perfect Classical Solutions, de Boer and Gorter (1950 a and b) and of Heer and Daunt (1951).

Experimental measurements by Sommers (1951 a and b and private communication) are shown by the points.

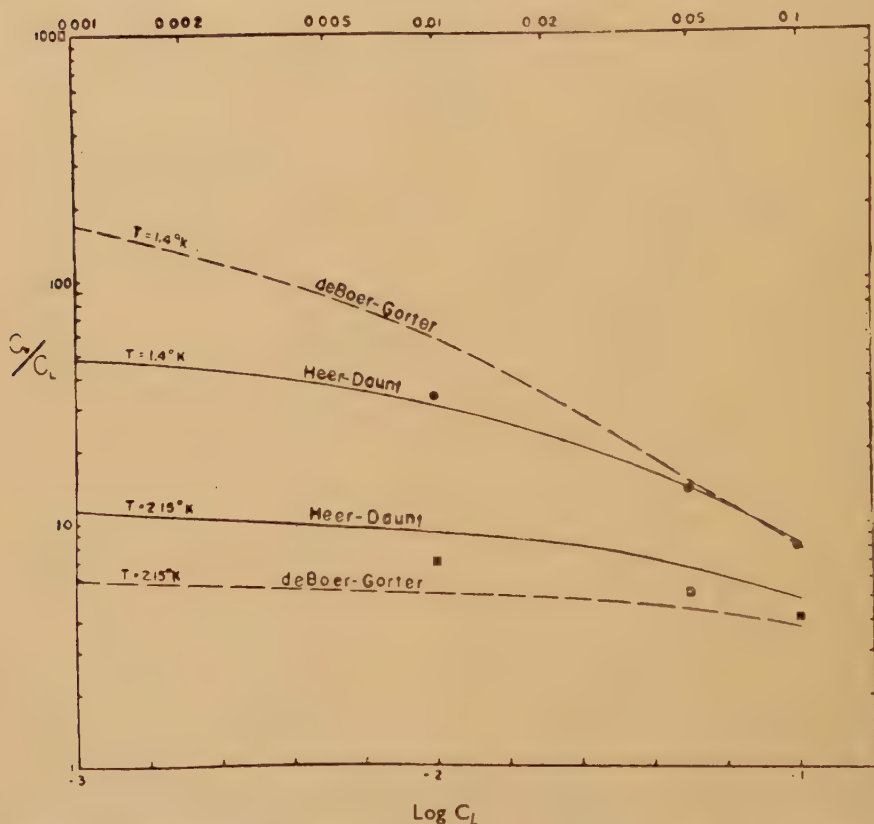
The writer is indebted to Dr. Sommers for permission to use his results here before full publication.

This is opposite to what would be expected according to the phase rule, which would, as pointed out above, predict that at temperatures below the λ -temperature of the richest solution, the measured vapour pressures

of the two solutions should become identical. It was concluded therefore that solutions of ^3He in liquid ^4He do not show phase separation, at least down to 1.04°K , and that therefore the λ -transition is always of second order.

Another theory of solutions of ^3He in ^4He , from which the numerical values of C_v/C_L have been calculated, has been put forward by Heer and Daunt (1951). The authors started from the basic theory of F. London (1938 a and 1938 b) which identified the λ -transition of helium I into helium II with the degeneracy of a perfect Bose-Einstein gas. They

Fig. 22



Plot of the distribution coefficient, C_v/C_L , for solutions of ^3He in liquid ^4He against the solution concentration, C_L , along two isothermals. (At 1.4°K and 2.15°K .)

The curves are the results of computations by Daunt, Tseng and Heer (1952) using the theories (as marked in the diagram) of de Boer and Gorter (1950 a and b) and of Heer and Daunt (1951).

The experimental measurements are shown by the points. The points at $C_L = 0.01$ are due to Daunt and Heer (1952) and to Sommers (1951 a and b). The points at the higher concentrations are due to Sommers (1951 b and private communication). The writer is indebted to Dr. Sommers for permission to use his results here before full publication.

assumed that liquid ^4He could be regarded as a perfect B-E gas situated in a smoothed potential well of depth $-\chi_4^0$ and that liquid ^3He could be regarded as a perfect Fermi-Dirac gas in a smoothed potential well of depth $-\chi_3^0$. For the solutions, the two components were regarded as statistically independent, and the total volume V of the solution and the total potential χ written as :

$$\left. \begin{aligned} V &= N_4 v_4^0 + N_3 v_3^0, \\ \chi &= N_4 \chi_4^0 + N_3 \chi_3^0, \end{aligned} \right\} \quad \dots \quad (16)$$

where v_4^0 and v_3^0 are the volumes per atom of ^4He and ^3He respectively. The Gibbs function, G , for the solution was approximated by the Helmholtz free energy, F , and could be written from the usual statistical methods as : $G \approx F = F_3 + F_4$, where

$$\left. \begin{aligned} \frac{F_3}{kT} &= N_3 \ln \lambda_3 - 4\pi \left(\frac{2m_3 kT}{h^2} \right)^{3/2} (N_3 v_3^0 + N_4 v_4^0) \int_0^\infty \ln(1 + \lambda_3^* e^{-y}) y^{1/2} dy \\ \text{and} \\ \frac{F_4}{kT} &= \ln(1 - \lambda_4^*) + N_4 \ln \lambda_4 + 2\pi \left(\frac{2m_4 kT}{h^2} \right)^{3/2} \\ &\quad (N_3 v_3^0 + N_4 v_4^0) \int_0^\infty \ln(1 - \lambda_4^* e^{-y}) y^{1/2} dy, \end{aligned} \right\} \quad \dots \quad (17)$$

where λ_3 and λ_4 are the degeneracy parameters appropriate to the number density and temperature of the ^3He and ^4He respectively. The terms λ_3^* and λ_4^* are given by $\lambda_3^* = \lambda_3 \exp(\chi_3^0/kT)$ and $\lambda_4^* = \lambda_4 \exp(\chi_4^0/kT)$. To calculate the vapour pressures from the Gibbs function given above, one further assumption had to be made regarding the degeneracy of the F-D component (the ^3He). For a perfect Fermi-Dirac gas with the number density given by that of pure liquid ^3He , the degeneracy temperature T^* is 4.85°K . In the calculations it was assumed therefore that as a first approximation in solution the ^3He could be treated as a Maxwell-Boltzmann assembly. (Detailed and explicit expressions were given by Heer and Daunt (1951) for the partial vapour pressure of the ^3He in solution when the ^3He was considered to be degenerate, but in view of the lack of knowledge of the value of T^* , no numerical calculations have been made from them. It was considered from internal evidence that T^* is probably less than 2°K .) With this assumption the calculation of the partial vapour pressures was straightforward, being dependent first on the calculation of the partial potentials, μ_3^L , μ_4^L and μ_3^v , μ_4^v (see above for notation) and then on the application of the condition for equilibrium between the liquid and vapour phases, as is set out in eqn. (12) above. Having calculated the partial vapour pressures, the values of C_v/C_L were obtained at once. The results for C_v/C_L for *dilute* solutions were :

Above the λ -temperature, T_λ^s , of the solution :

$$\frac{C_v}{C_L} = \frac{p_3^0 v_3^0}{p_4^0 v_4^0} \exp \left[1 - \frac{v_3^0}{v_4^0} \left\{ 1 - 0.462 \left(\frac{T_\lambda^s}{T} \right)^{3/2} - 0.022 \left(\frac{T_\lambda^s}{T} \right)^3 - \dots \right\} \right]. \quad (18a)$$

Below the λ -temperature, T_λ^s , of the solution :

$$\frac{C_v}{C_L} = \frac{p_3^0 v_3^0}{p_4^0 v_4^0} \exp \left[1 - 0.514 \left(\frac{T}{T_\lambda^s} \right)^{3/2} \frac{v_3^0}{v_4^0} \right]. \quad (18b)$$

It will be seen that there are no arbitrary adjustable parameters involved in the equations for C_v/C_L . v_3^0 and v_4^0 are obtained directly from the known molar volumes of pure liquid helium III and pure liquid helium IV. The values of C_v/C_L according to eqns. (18a) and (18b) have been computed and are given by the full curve of fig. 6. It will be seen that the observed trend for C_v/C_L for very dilute solutions to be much larger than the values given by Raoult's law below T_λ^s is accounted for by the theory. It is to be noted also that the slope of the curve is continuous across the λ -temperature, and that the theory predicts somewhat higher values of C_v/C_L than those calculable from Raoult's law even *above* T_λ . Computations have been made of C_v/C_L for more concentrated solutions by Daunt, Tseng and Heer (1952) and the results of these for solution concentrations of 1.00, 1.65, 5.00 and 10.00% are shown by the full curves in figs. 11, 19, 20 and 21. Also isothermal curves showing the variation of C_v/C_L with C_L according to the theory are given in fig. 22 from computations by Daunt, Tseng and Heer. It will be seen that for all concentrations the theory gives values of C_v/C_L greater than those calculable from the laws for perfect classical solutions, although the differences are less marked for the higher concentrations.

In the calculations outlined above it was assumed that the ^3He was a non-degenerate Fermi-Dirac liquid. If however it is assumed that as a pure liquid the ^3He is degenerate, although in solution it is non-degenerate (a situation which is very likely in the temperature range 0.5°K up for solutions of $C_L \leq 20\%$), then the results for the vapour pressures etc. given above need modification. These modifications have been investigated by Heer and Daunt (1951), and it was shown that for T less than about one quarter of the pure liquid ^3He degeneracy temperature, T^{*0} ,

$$\frac{C_v}{C_L} = \frac{p_3^0}{p_4^0} \cdot \frac{v_3^0}{v_4^0} \cdot \frac{4\pi^{1/2}}{3} \left(\frac{T^{*0}}{T} \right)^{3/2} \exp \left[-\frac{3}{5} \frac{T^{*0}}{T} + \frac{\pi^2}{4} \frac{T}{T^{*0}} - 0.514 \left(\frac{T}{T_\lambda^s} \right)^{3/2} \frac{v_3^0}{v_4^0} \right]. \quad (19)$$

At sufficiently low temperatures the term $\exp [-\frac{3}{5} (T^{*0}/T)]$ predominates and results in a reduction in the values of C_v/C_L , even *below* the values calculable for perfect classical solutions. For still higher concentrations of ^3He in solution and/or at lower temperatures, the ^3He in solution must be considered degenerate. Such a condition has also been considered by Heer and Daunt (1951), and it was found to result also in a lowering of the calculated C_v/C_L *below* that given for perfect classical solutions at sufficiently low temperatures. The general conclusion that is obtained from these computations is that for solutions up to about 20% concentration the computations illustrated in figs. 11, 19, 20, 21 and 22, based on non-degenerate F-D statistics are valid for temperatures above about 1.0°K . For higher concentrations or at temperatures below about 1.0°K , however,

the effects of degeneracy in the F-D system must be taken into account, and the results will show that C_v/C_L lies below the perfect classical solution value at low temperature.

Figs. 6, 11, 19, 20 and 21 show the experimental measurements of C_v/C_L for various concentrations. It will be seen that below the λ -temperatures of the solutions, T_λ^* , both the theories of de Boer and Gorter and of Heer and Daunt are in broad agreement with experiment. It would appear that Heer and Daunt's theory fits the facts well, especially at low temperatures. (See also fig. 22.) It should be noticed, however, that at the higher temperatures plotted the experimental results lie between the values calculated from the two theories. In the higher temperature range of the measurements (say 1.8°K to 2.2°K and higher) the vapour is dense and far from perfect. On the other hand the numerical computations from the theories have been made assuming throughout perfect vapours. If the non-ideality of the vapour phase were to be taken into account in the theoretical computations, then, as Kilpatrick (1950) has shown, (see below and table 9), the computed C_v/C_L is reduced. Such a reduction in the theoretical C_v/C_L values at the higher temperatures would make the theory of Heer and Daunt approximate more nearly the experimental results. For a further test of the theory, more experimental measurements at temperatures above 2.2°K would be of great value.*

Table 9. Values of the Partial Vapour Pressures of a 1.0% Solution of ^3He in Liquid ^4He and Values of C_v/C_L , as Calculated by Kilpatrick (1950), from de Boer and Gorter's (1950 a and b) Theory Taking Account of the Imperfections in the Vapour Phase

$T^\circ \text{K}$	Real Vapour			Ideal Vapour		
	$p_4(\text{mm})$	$p_3(\text{mm})$	C_v/C_L	$p_4(\text{mm})$	$p_3(\text{mm})$	C_v/C_L
2.4	62.08	2.51	3.89	61.96	2.91	4.49
2.3	49.78	2.20	4.23	49.69	2.54	4.86
2.2	39.22	1.87	4.55	39.15	2.13	5.16
2.1	30.61	1.86	5.73	30.55	2.11	6.46
2.0	23.22	2.02	8.08	23.16	2.27	8.93
1.9	17.15	2.22	11.46	17.09	2.48	12.67

It is to be noted that in all the calculations of C_v/C_L described above, the vapour phase was assumed throughout to be perfect. An estimate of the error involved in making this assumption has been made by Kilpatrick (1950) who has applied corrections involving the second virial coefficient in the equation of state for the vapour to the theory of De Boer and Gorter (1950 a and 1950 b). Kilpatrick used the values calculated by van Kranendonk, Compaan and de Boer (1949) for the second virial coefficient, B_3 , of pure ^3He and for the cross second virial coefficient, B_{34} , he took the

* A paper on C_v/C_L measurements by Eselson and Lazarew (1950 d) has recently been noted in *Science Abstracts*. Insufficient data on it, however, are at present available to the writer.

arithmetic mean of B_3 and B_4 . His results are shown in table 9 which gives the numerical values of the partial pressures p_3 and p_4 and of C_v/C_L for a 1.00% solution in the temperature range 1.9° K to 2.4° K. It will be seen from table 9 that the effect of gas imperfection is to decrease p_3 and C_v/C_L and to increase p_4 slightly. From these results it would appear that in the temperature range from about 1.8° K up to the λ -temperature of ^4He corrections of about 10% should be made to the calculated values of C_v/C_L . In view of the arbitrary assumption as to G_4 , the Gibbs function for pure liquid ^4He , in the theory of de Boer and Gorter, in view of the necessarily simplifying assumptions as to perfect B-E and F-D liquids in the theory of Heer and Daunt and in view of the possible lack of precision in the experimental measurements of C_v/C_L , it is doubtful whether the process of correction for vapour imperfections is worth while, at least below the λ -temperature of ^4He .

(c) *Partial Vapour Pressures*

The partial vapour pressures over solutions of ^3He in liquid ^4He can be calculated using the theories of de Boer and Gorter and of Heer and Daunt in the manner outlined in the section above. The results of one such computation (Daunt, Tseng and Heer 1952) are shown in fig. 23 in which the total vapour pressure, $P = p_3 + p_4$, is plotted against temperature for a 20% solution according to these two theories and according to the laws for perfect classical solutions. Experimental measurements have been made of the vapour pressure of a 20.3% solution by Weinstock, Osborne and Abraham (1950) and their results are also shown in fig. 23. It will be seen that the experimental values are higher than those calculated for perfect classical solutions over the whole temperature range measured ($1.05^\circ < T < 3.2^\circ \text{ K}$). It will be seen also that the values calculated according to the theory of Heer and Daunt follow very accurately the observed results at temperatures below 1.8° K. Above 1.8° K the agreement is not exact, but the trend is qualitatively correct.

(d) *The Change in λ -temperature*

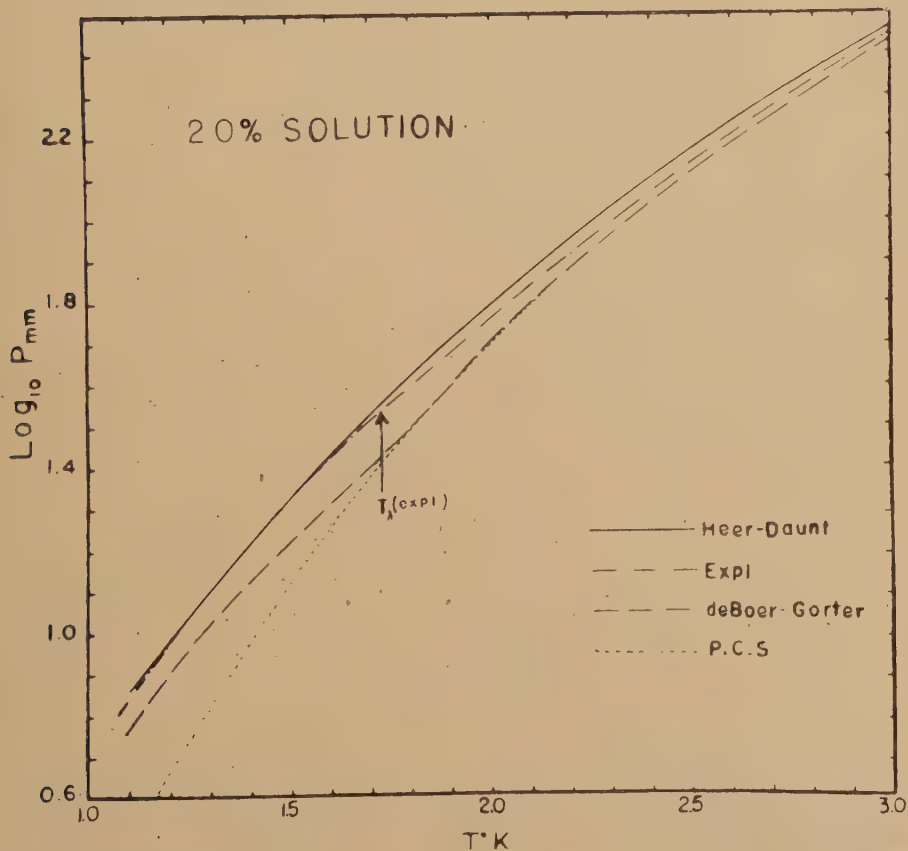
The laws for perfect classical solutions give for the Gibbs function, G :

$$G = (1-X)G_4 + XG_3 + RT\{X \ln X + (1-X) \ln (1-X)\} \quad . \quad . \quad (20)$$

where $X = C_L$, the solution concentration. Thermodynamically it can be shown, as is evident from the work of Stout (1948) (the specialized applications of the general thermodynamic formulae given in Stout's paper were based on preliminary and unreliable experimental evaluations of C_v/C_L , and can be disregarded), that eqn. (20) leads to the conclusion that the λ -transformation of helium I into helium II remains second order for all ^3He concentrations and that its λ -temperature, 2.18° K, would be independent of ^3He concentration. In order to account for the observed change in the λ -transformation temperature, T_λ^s , using classical thermodynamics it is necessary to inject a reflection of the quantum nature of liquid helium through some experimentally observed phenomenon. The

required phenomenon to hand is the hypothesis put forward by Taconis *et al.* (1949 a and 1949 b), namely that the ^3He can be regarded as being in solution with the 'normal' constituent of the helium II only. With this the classical eqn. (20) for the Gibbs function becomes changed to the eqn. (10), and from this a thermodynamic evaluation of the change of T_λ^s with X can be made, as has been done by de Boer (1949), de Boer and Gorter (1950 a and 1950 b), Stout (1949). A different approach has been made by Rice and co-workers (see Rice 1949, Engel and Rice 1950, Rice 1950 a and 1950 b, Rice and Engel 1950, Morrow 1951). In the work of these authors it is assumed that in helium II the superfluid and normal constituents of

Fig. 23



Plot of the vapour pressure of a 20% solution of ^3He in liquid ^4He against temperature.

Three of the curves (as marked in the diagram) are the results of computations by Daunt, Tseng and Heer (1952) and by Heer and Daunt (1951) using the theories of Perfect Classical Solutions, of de Boer and Gorter (1950 a and b) and of Heer and Daunt (1951).

A curve showing the experimental results of measurement of the vapour pressure of a 20.3% solution by Weinstock, Osborne and Abraham (1950) is also given.

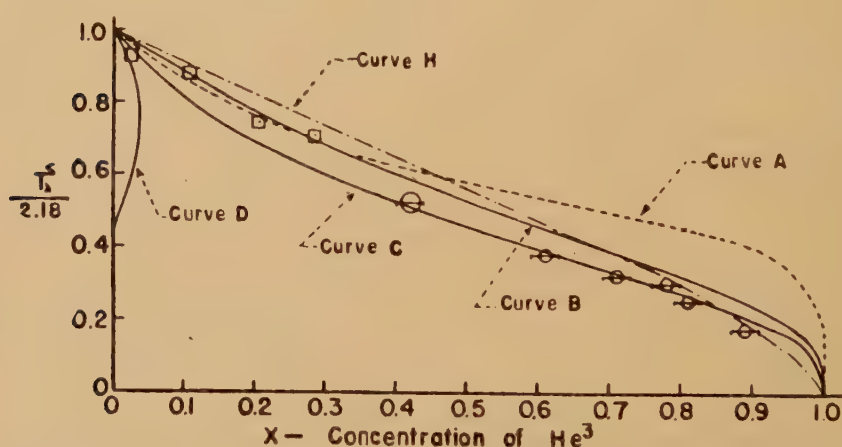
the two-fluid model can be treated as two separate phases *separated in configurational space* with the superfluid phase having possibly a 'fibroid' structure and that these phases can be described by classical thermodynamics. As in the work of de Boer, Gorter and Stout, Rice and co-workers introduce the quantum nature of $^3\text{He} + ^4\text{He}$ solutions by assuming Taconis' hypothesis. An outline of this work is given below.

In the theory of de Boer (see de Boer 1949 and de Boer and Gorter 1950 a and 1950 b (case B)) the assumptions, as outlined in § 5(b) above, lead to the conclusion that below the λ -temperature of the solution, T_λ^s , the $^3\text{He} + ^4\text{He}$ mixture separates into two phases, a helium I phase and a helium II phase. The calculations indicate, moreover, that variation of T_λ^s with ^3He concentration, X , for X tending to zero is given by :

$$(\partial T_\lambda^s / \partial X)_{X \rightarrow 0} \approx -2RT_\lambda / S_\lambda = -5.46, \quad \dots \quad (21)$$

so yielding a numerical value which is approximately twice that of the observed value. The full curves are shown in fig. 24.

Fig. 24



Plot of the λ -temperature, T_λ^s , of solutions of ^3He in liquid ^4He as a function of the solution concentration, X .

Curve A is obtained from Stout's (1949) theory.

Curve B is obtained from de Boer and Gorter's (1950 a and b) theory. (G_4 linear in T .)

Curves C and D are obtained from de Boer's theory (1949) for phase separating solutions.

Curve H is obtained from Heer and Daunt's (1951) theory, and is the same as that given in fig. 4.

The points show the experimental results, as detailed in fig. 4.

In the theory of de Boer and Gorter (case A) (1950 a and 1950 b), eqn. (11) above, giving the equilibrium minimum value of G , gives at once the value of T_λ^s , if in it x is put equal to 1 (i.e. for zero superfluid

fraction) and if, in consequence, X_e is put equal to X . The equation for the T_{λ}^s line therefore becomes :

$$1-X = \exp \left[- \left(\frac{\partial G_4}{\partial x} \right)_T / RT_{\lambda}^s \right]_{x=1}, \quad . . . \quad (22)$$

or, using eqn. (14) :

$$1-X = \exp [S_{\lambda}(T_{\lambda}^s - T_{\lambda})/RT_{\lambda}^s]. \quad . . . \quad (23)$$

For $X \rightarrow 0$, eqn. (23) reduces to :

$$(\partial T_{\lambda}^s / \partial X)_{X \rightarrow 0} \approx -RT_{\lambda}/S_{\lambda} = -2.73, \quad . . . \quad (24)$$

so yielding a numerical value in close agreement with experiment. A graph showing eqn. (23) is given in fig. 24, which also shows the experimental points.

Using essentially the same assumptions, together with the assumption that the discontinuity in the specific heat at the λ -temperature of pure ^4He , ΔC_p^4 , remains constant and independent of the solution concentration, Stout (1948 and 1949) arrived at the formulation for the T_{λ}^s line :

$$dT_{\lambda}^s/dX = -T_{\lambda}^s[X(1-X)(1+6X) + (1-X)7.6/6R], \quad . . \quad (25)$$

which is graphically illustrated in fig. 24. It will be seen that whereas the agreement with experiment is good for low ^3He concentrations, Stout's curve diverges from the observed results for high concentrations. This is probably due to the fact that the assumption of a concentration invariant ΔC_p^4 is an approximation valid only for low concentration.

The numerical evaluation of the T_{λ}^s line from de Boer and Gorter's eqn. (22), is, of course, dependent on the assumptions made regarding G_4 as a function of T and x . The choice made by de Boer and Gorter (see eqn. (14)), involving a linear function of T , would give at $T=T_{\lambda}$ a zero specific heat for helium I. Another choice has been suggested by de Boer (1949), who proposed a quadratic function for the term in T . Under the conditions expressed in eqn. (15), such a quadratic function yields for G_4 :

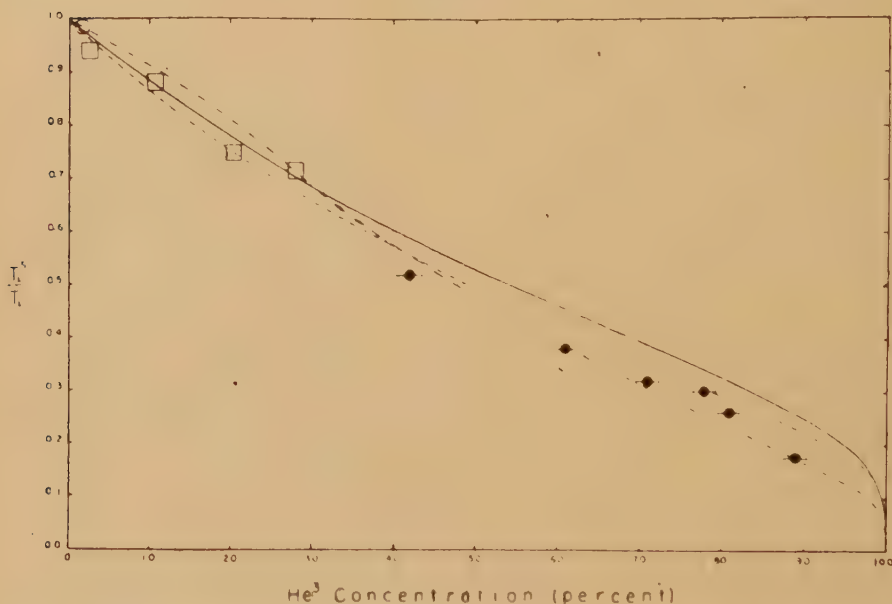
$$G_4 = -E_0(1-x^{7/6}) - \frac{1}{2} \frac{S_{\lambda}}{T_{\lambda}} x^{5/6} T^2. \quad . . . \quad (26)$$

This equation for G_4 makes the entropy of helium I *linearly* proportional to T , an experimental fact which had previously been pointed out by Daunt and Mendelssohn (1946). A computation of the T_{λ}^s line as a function of X , using eqn. (26), has been made by the writer and the result is shown in fig. 25, which also shows the experimental points. From fig. 25 it will be seen that both the linear eqn. (14) and the quadratic eqn. (26) are in moderate agreement with the observations, the one curve being in good agreement at the lower concentrations and the other at the higher concentrations. A further discussion of possible expressions for G_4 in relation to the T_{λ}^s line has been given by Daunt and Heer (1950).

Rice (1949) has proposed a two-fluid theory envisaging a separation of the superfluid and the normal fluid in configurational space into two phases, the superfluid being of a 'fibroid' structure. A separation of the superfluid and normal fluid in configurational space for dilute solutions of ^3He in ^4He had previously been proposed by London and Rice (1948) in explanation of experimental results for C_v/C_L by Fairbank *et al.* (1947 and 1948). These results were subsequently shown not to be representative of the equilibrium properties of ^3He solutions (see § 3(c)).

Rice and Engel (see Rice 1949, Engel and Rice 1950, Rice 1950 a, b, Rice and Engel 1950) have developed the thermodynamics of Rice's theory to describe the behaviour of solutions of ^3He in ^4He . Classical thermodynamics were applied to the phase separating system under the following basic assumptions: (a) the partial molar enthalpy \bar{H}_{4s} of the superfluid was set equal to zero, (b) the λ -temperature is the temperature at which the chemical potential of the superfluid helium at zero concentration becomes equal to the chemical potential of the normal

Fig. 25



Plot of the λ -temperature, T_λ^s , of solutions of ^3He in liquid ^4He as a function of the solution concentration, X , as computed from various theories.

The curve marked ————— is computed from the theory of de Boer and Gorter (1950 a and b), using a linear function of temperature for the Gibbs function, G_4 . (See eqn. (14)).

The curve marked - - - - - is computed also from the theory of de Boer and Gorter (1950 a and b), using a quadratic function of temperature for the Gibbs function, G_4 . (See eqn. (26)).

The curve marked - . - . - . is computed from the theory of Rice (1950 b), using assumptions as mentioned in the text.

fluid, (c) Taconis's hypothesis was assumed, and (d) the solutions were assumed perfect. This model then led to the following evaluation for the T_λ^s line :

$$\frac{dT_\lambda^s}{dX} = -\frac{1}{R}(RT_\lambda^s)^2/\bar{H}_{4n\lambda}(1-X), \quad (27)$$

where $\bar{H}_{4n\lambda}$ is the partial molal enthalpy of the normal fluid at T_λ^s . For dilute solutions, using Tisza's relation (eqn. (15)), this reduces to :

$$\left(\frac{\partial T_\lambda^s}{\partial X}\right)_{X \rightarrow 0} = -\frac{7}{6}RT_\lambda/S_\lambda, \quad (28)$$

which will be seen to be the same as eqn. (24) except for the numerical coefficient 7/6.

The authors have made many computations of the T_λ^s line numerically from eqn. (27), one of which is shown in fig. 25 for the case where \bar{H}_{4n} is taken to be constant and equal to 2.95 cal/mole and where \bar{S}_{4n} also is taken to be constant and equal to S_λ . This curve has been chosen as the one that fits most closely the experimental points under the general assumptions (a) to (d) given above. A discussion of various T_λ^s lines deducible under different assumptions with regard to the normal fluid below T_λ and under conditions of non-ideality of the solutions has been given by Morrow (1951).

The absence of any notable difference between the values measured in helium I and in helium II of the electric polarizability (Wolfke and Keesom 1928 a, b, and Grebenkemper and Hagen 1950), of the optical refractivity (Johns and Wilhelm 1938), or of the x-ray structure (Keesom and Taconis 1938, Reekie 1940, 1947), appears to indicate an absence of molecular association or of structure changes in liquid helium in the transformation from helium I to helium II. Nevertheless Rice's model, involving phase separation in configurational space, leads to an evaluation of the T_λ^s line for $^3\text{He}+^4\text{He}$ solutions in fair quantitative agreement with experiment (see fig. 25). Moreover, it will be seen that widely different assumptions for the Gibbs function, G_λ , of pure liquid helium four, as embodied in eqns. (14) and (26), provide through the thermodynamic theory of de Boer and Gorter evaluations of the T_λ^s line which are not widely different from one another (see fig. 25 also). It is concluded that the predominating influence on all these evaluations is the Taconis hypothesis, whereby the quantum nature of the liquid is introduced in the classical thermodynamics.

The quasi-gaseous model for solutions of ^3He in ^4He of Heer and Daunt (1951), outlined in § 5 (b) above, also allows an evaluation of the T_λ^s line. The degeneracy temperature of a perfect Bose-Einstein (^4He) fluid is given by :

$$T_\lambda = (h^2/2\pi m_4 k)(1/2.612 v_4^0)^{2/3}, \quad (29)$$

which yields a value of 3.13° K when v_4^0 is determined by the liquid density of ^4He , as was pointed out by London (1938 a, b), which is surprisingly close to $T_\lambda = 2.18^\circ \text{K}$.

Assuming statistical independence of the B-E and F-D systems in solutions of ^3He in ^4He , Heer and Daunt showed that the λ -temperature, T_λ^s , of the solution is given by the degeneracy temperature of the B-E system (^4He), namely by :

$$T_\lambda^s = (h^2/2\pi m_4 k)(1/2 \cdot 612)^{2/3} [N_4/(N_3 v_3^0 + N_4 v_4^0)]^{2/3}, \quad \dots \quad (30)$$

i.e. T_λ^s is determined by the ^4He number density and the temperature only, as was pointed out initially by Daunt and Heer (1950). Combining the eqns. (29) and (30), one gets :

$$\begin{aligned} T_\lambda^s/T_\lambda &= [N_4 v_4^0/(N_3 v_3^0 + N_4 v_4^0)]^{2/3} \\ &= \left[\frac{\text{Mol. vol. of pure liquid } ^4\text{He}}{\text{Mol. vol. of solution}} \right]^{2/3}, \quad \dots \quad (31) \end{aligned}$$

or in terms of the ^3He concentration, X ,

$$\frac{T_\lambda^s}{T_\lambda} = \left[\frac{1-X}{1+X(v_3^0/v_4^0-1)} \right]^{2/3} \quad \dots \quad (32)$$

It will be seen that there are no adjustable parameters involved. A plot of T_λ^s/T_λ is given in fig. 4, which has been computed by taking v_3^0 and v_4^0 to be given by the known molar volumes of ^3He and ^4He in the liquid phase. The general agreement between theory and experiment evident in fig. 4 is good, in spite of the somewhat simple nature of the theoretical assumptions. It suggests that the quantum statistical approach to the λ -phenomenon in liquids is at least a satisfactory first approximation and that the type of statistics plays a predominant role in determining the occurrence of superfluidity, as was first maintained by London. It is of interest that quantum thermodynamics leads to an adequate explanation of many of the properties of $^3\text{He} + ^4\text{He}$ solutions in this way *without* recourse to the assumption made in Taconis' hypothesis. The relation between this theory and Taconis' hypothesis has been discussed by Daunt, Tseng and Heer (1952).

Another statistical model of $^3\text{He} + ^4\text{He}$ solutions has been put forward by Harasima (1951), who has obtained an evaluation of the T_λ^s line as a function of ^3He concentration. Harasima regards the solution as a mixture of Bose-Einstein and Fermi-Dirac systems, for which the liquid incompressibility is accounted for, as in the theory of Heer and Daunt, by assuming a constant volume attached to each particle. The basic assumptions differ, however, somewhat from those of Heer and Daunt, in that Harasima assumes (a) that the volume per atom is the same for ^3He as for ^4He , (b) that the Bose-Einstein system is not perfect, but is modified by the introduction of an energy gap, ϵ_0 , between the lowest energy level and the remainder of the energy spectrum (this is similar to the modifications which have been suggested by Bijl, de Boer and Michels 1941, and by Goldstein 1946), and (c) that the volume in which the F-D system (the ^3He) can move is only that volume *not* occupied by the superfluid atoms. Assumption (c) reaches further than

the usual statement of Taconis' hypothesis, and essentially implies a phase separation similar to the theory of Rice. From statistical considerations Harasima then arrives at an expression for the T_λ^s line, namely :

$$\frac{T_\lambda^s}{T_\lambda} = (1-X)^{2/3} F(\epsilon_0/kT_\lambda) / F\left(\frac{\epsilon_0}{kT_\lambda^s} - \frac{2}{3} \cdot X \cdot \frac{F_{1/2}(\alpha)}{F_{3/2}(\alpha)}\right), \quad . \quad . \quad (33)$$

where

$$F(\eta) = \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{x^{1/2} dx}{e^{\eta+x} - 1},$$

and where α describes the usual degeneracy parameter, $e^{-\alpha}$, for a F-D distribution function. In evaluating T_λ^s from eqn. (33), the term ϵ_0 is an adjustable parameter. α is not adjustable, since the F-D system was assumed perfect. Harasima found that with a value of the energy gap, ϵ_0 , equal to $0.40 kT_\lambda$, that the T_λ^s line fitted within experimental error all the observations. It appears to the writer that the theory is weakened by imposing on it the *ad hoc* modification of Taconis' hypothesis, for which no theoretical justification is given, and which should presumably be an end-product of any molecular theory.

Since so many theories of the T_λ^s line are extant, it is thought to be of interest to compare their predictions, at least so far as the initial slope of the T_λ^s line is concerned, in tabular form. This comparison is given in table 10.

Table 10. Values of the Slope of the Curve for the λ -temperature, T_λ^s , of Solutions of ^3He in ^4He against Solution Concentration, X , for Zero ^3He Concentration

Order of transition	Reference	Theory	Comments
		$(dT_\lambda^s/dX)_{X \rightarrow 0}$ deg./mole fraction	
1st	de Boer (1949)	-5.46	
1st	Stout (1949)	-6.8	
2nd	Stout (1949)	-3.4	
2nd	de Boer and Gorter (1950 a and b).	-2.73	For G_4 linear in T
2nd	ditto.	-1.6	For G_4 quadratic in T
2nd	Rice (1949)	-3.16	
2nd	Heer and Daunt (1951)	-1.95	
2nd	Harasima (1951)	-2.6	
<i>Experiment</i>			
	Abraham <i>et al.</i> (1949)	-2.8 approx.	
	Eselson and Lazarew (1950 b)	-2.0	

Note added in proof.—A recent paper by Toda and Isihara (*Prog. of Theor. Phys.*, **6**, 480, 1951) considers theoretically the change of λ -temperature, T_λ^s , of solutions of ^3He in liquid ^4He as a function of the solution concentration, X . They give a classical thermodynamic treatment, similar to that of de Boer and Gorter (1950 a and b), into which they insert the Taconis' hypothesis. As pointed out in section 5 (d) above,

the subsequent numerical development depends on making an arbitrary choice for G_4 , the Gibbs free energy for pure liquid ${}^4\text{He}$, and for this Toda and Ishihara propose first a phenomenological expression somewhat different from eqns. (14) and (26) above but which, with a suitable choice of the adjustable parameters, leads to an evaluation of the T_λ^s line in fair agreement with experiment.

Secondly they employ the molecular model of liquid ${}^4\text{He}$ proposed by Toda (*Prog. of Theor. Phys.*, **6**, 458, 1951) to provide an alternative expression for the free energy of pure liquid ${}^4\text{He}$. This expression for the free energy involves a thermal excitation quantum, Δ , as in the roton spectrum of Landau's theory (Landau, 1941, 1944), and by choosing $\Delta/k=8.7^\circ\text{K}$, Toda and Ishihara computed a T_λ^s line in approximate agreement with experiment. The results of these computations appear to the writer to emphasize the conclusion already presented above, namely that in all evaluations of the T_λ^s line (and other thermodynamic properties) using classical thermodynamics the predominating influence is the Taconis hypothesis whereby the quantum nature of the liquid ${}^4\text{He}$ is injected into the calculations, and whereby approximating agreement with experiment is obtained almost irrespective of assumed variations in the energy spectrum of pure liquid ${}^4\text{He}$.

(e) Viscosity

Statistical models in which ${}^3\text{He}$ in solution is assessed to have the properties of a perfect Fermi-Dirac gas have been put forward by ter Haar and Wergeland (1949) and by Singwi and Kothari (1949) to predict the viscosity of solutions of ${}^3\text{He}$ in ${}^4\text{He}$ at various temperatures. ter Haar and Wergeland supposed that, at least for dilute solutions, the total viscosity could be regarded as the sum of separate viscosities of the ${}^3\text{He}$ and the ${}^4\text{He}$ taken separately, and in order to make their calculations they assumed that on mixing the spacing of the atoms remained the same, i.e. they assumed $\rho_3/m_3=\rho_4/m_4$. The kinetic viscosity of the ${}^3\text{He}$, they stated, would be much larger than that for ${}^4\text{He}$, since they regarded the ${}^3\text{He}$ as a F-D gas, and it would remain temperature independent. Under these assumptions, numerical computations were made for a 1.0% solution of ${}^3\text{He}$ in ${}^4\text{He}$.

The paper of ter Haar and Wergeland has been criticized by Singwi and Kothari (1949), who pointed out that the viscosity of a F-D gas would not be temperature independent but would instead increase markedly as the temperature is reduced owing to the increasing mean free path. Such an increasing mean free path with decreasing temperature is due to the fact that in a degenerate F-D gas, a reduction in temperature causes a reduction in the number of effective collisions due to the Pauli exclusion principle. Using the same assumptions as ter Haar and Wergeland, Singwi and Kothari express the ${}^3\text{He}$ viscosity by :

$$\eta_3 = \alpha \frac{1}{3} \frac{h^5}{2^{5/2} m_3^2} \left(\frac{3\rho_4}{8\pi m_4} \right)^{5/3} \frac{1}{S} \frac{1}{(kT)^2}, \quad \dots \dots (34)$$

where S is the collision cross section, α a numerical constant, and where the quantities involving ${}^4\text{He}$ are introduced through the assumption that $\rho_3/m_3 = \rho_4/m_4$, i.e. of equal spacing of atoms in the solution. This expression is essentially the same as that derived for degenerate F-D gases by Tomonaga (1938). Again numerical computations were made for the viscosity of a 1.0% solution of ${}^3\text{He}$ in ${}^4\text{He}$. In view of the fact that no experimental data are available on the viscosity of ${}^3\text{He}$ in ${}^4\text{He}$ solution, these numerical results are not quoted. Moreover it is not clear that the treatment of the ${}^3\text{He}$ in dilute solution as a degenerate F-D gas is justifiable. For pure liquid ${}^3\text{He}$, its liquid density would give a degeneracy temperature of 4.85°K , if it were assumed to be a perfect F-D gas; so that for dilute solutions the degeneracy temperature would be below any convenient operating range (assuming, as seems evident from the work of Heer and Daunt (1951), that the ${}^3\text{He}$ and ${}^4\text{He}$ in solution are statistically independent systems).

(f) *Second Sound*

A theory for the variation of the velocity of second sound with concentration and temperature in solutions of ${}^3\text{He}$ in liquid ${}^4\text{He}$ has been given by Pomeranchuk (1949). Pomeranchuk considered the effect of adding impurities in small concentration to liquid ${}^4\text{He}$, and treated ${}^3\text{He}$ in solution as a special case for one kind of impurity. First he considered that the impurity would be associated with the 'normal' constituent of the helium II only, and wrote for the total 'normal' density, ρ_n :

$$\rho_n = \rho_{n0} + \rho_{ni}, \quad \dots \quad (35)$$

where ρ_{n0} is the density of the 'normal' constituent of the pure liquid ${}^4\text{He}$ and ρ_{ni} the impurity density. Then he limited his considerations to *small* concentrations, in which the concentration, ϵ , by *weight* of the impurity was less than 1%. For such concentrations the assembly of impurities was treated statistically as an independent assembly obeying classical statistics, such that the energy spectrum could be written as:

$$\left. \begin{array}{l} \text{Case (a)} \quad E = E_0 + p^2/2\mu, \\ \text{or Case (b)} \quad E = E_0 + (p - p_0)^2/2\mu, \end{array} \right\} \quad \dots \quad (36)$$

where μ is the effective mass of the extraneous particle in solution and where p_0 is, in Case (b), the momentum for which the energy is a minimum.

Pomeranchuk showed that the impurity density, ρ_{ni} , for Case (a) would be $\rho_{ni} = \rho \epsilon \mu / m_i$, and for Case (b), above a certain characteristic temperature given by the interaction energy between the impurities, $\rho_{ni} = \rho \epsilon p_0^2 / 3m_i kT$. For the entropy *per gramme* he wrote:*

$$S = (1 - \epsilon)S_0 + \epsilon S_i - \frac{k\epsilon}{m_i} \ln \epsilon, \quad \dots \quad (37)$$

* It would appear, in view of the success of Taconis' hypothesis when applying classical thermodynamics to mixtures of ${}^3\text{He}$ in liquid ${}^4\text{He}$, appropriate to use the hypothesis in calculation of the entropy of mixing.

where S_0 is the entropy per g of the pure liquid ^4He , S_i the entropy per g of the impurities taken in the 'pure' state (S_i is immediately given for both cases (a) and (b) by the usual classical statistical expression for perfect gases) and where the third term on the right-hand side of eqn. (37) is the usual entropy of mixing.

From the expressions derived for S_i , Pomeranchuk derived the specific heat of the solution, which was :

$$\left. \begin{array}{l} \text{for Case (a)} \\ \text{for Case (b)} \end{array} \right\} \begin{array}{l} C = C_0 + 3k\epsilon/2m_i, \\ C = C_0 + k\epsilon/2m_i, \end{array} \quad (38)$$

where C_0 is the specific heat of pure liquid ^4He and where, as would be expected for a classical perfect gas of impurities, the second terms give the *constant* specific heat of the impurities.

Using the expressions given in eqns. (37) and (38) for S and C , Pomeranchuk was able to modify the usual expression for the velocity, u_2 , of second sound in *pure* helium II, which is given by :

$$u_2^2 = (\rho_s/\rho_n)(TS^2/C), \quad (39)$$

where ρ_s is the density of the superfluid constituent of helium II, and he derived for the second sound velocity, u_{2i} , in the presence of ^3He impurities, the expression

$$u_{2i}^2 = (\rho_s/\rho_n)[T(S_0 + k\epsilon/m_3)^2/C + Tk\epsilon/m_3]. \quad (40)$$

Numerical computation for dilute solutions shows that as the temperature is decreased below the λ -temperature, first u_{2i} takes on values *higher* than u_2 with the difference $(u_{2i} - u_2)$ increasing with increasing concentration, ϵ , in general qualitative agreement with the experimental results of Lynton and Fairbank (1950 a, b), (see § 3 (d) above) and secondly as the temperature is still further decreased the curves for u_{2i} and u_2 against temperature cross and u_{2i} tends to zero as T tends to zero. No experimental confirmation of this second process is as yet available.

In making numerical computations from eqn. (40) for u_{2i} , the hidden parameter μ is an adjustable constant. Both Lynton and Fairbank (1951) and Khalatnikow (1951) have made such numerical computations using Pomeranchuk's theory in order to obtain the best fit with the experimental results of Lynton and Fairbank. Khalatnikow found that for case (a), eqn. (40) fitted the experimental results over a wide range of temperature if the effective mass μ of the ^3He 'impurity' were taken to be approximately $2.8m_3$, i.e. 2.8 times the free mass of the ^3He atom. For case (b) on the other hand he found that no single value of μ would be appropriate over the entire temperature range, and consequently the energy spectrum describing case (b) is probably invalid. In a similar manner Lynton and Fairbank's computations led to a value of $\mu \approx 3.85m_3$ for the temperature range 1.4 to 1.9°K , but to explain the results at 1.25°K the theory required a value of $\mu \approx 3.3m_3$. No theoretical basis has been

suggested* for accounting for $\mu \neq m_3$, and it would appear that, in order to make the theory more secure, experimental measurements over a wider temperature range are desirable. Measurements in the temperature range below 1.0°K would be of extreme interest, for in this temperature region Pomeranchuk's theory predicts that, owing to the predominant role played by the impurities, the second sound velocity, u_{2i} , should fall numerically well below the value u_2 for pure helium II.

§ 6. THEORIES OF PURE LIQUID AND SOLID ^3He

(a) General Properties

It was first supposed by London and Rice (1948) on theoretical grounds that ^3He could not exist in the liquid state at any temperature and normal pressure. A similar view was expressed by Tisza (1948). It was considered that, since its zero-point energy would be higher than that for ^4He , the zero-points repulsion would more than compensate the van der Waals attractive forces, and consequently liquefaction would not occur.

A different and more detailed suggestion was put forward by de Boer and Lunbeck (1948 a, b), based on the quantum theory of condensed gases due to de Boer (1948). (See also, for further development of de Boer's theory of condensed gases, de Boer and Blaisse 1948, and de Boer and Lunbeck 1948 c.) This theory expresses all macroscopic quantities, as the temperature, molar volume, pressure or internal energy, in terms of molecular units which are derived from two characteristic quantities, namely the energy ϵ and a length σ which characterizes the intensity and range of the intermolecular potential field, which field between simple molecules is described by the function :

$$\phi(r) = \epsilon f(r/\sigma) = \epsilon \left\{ \frac{4}{(r/\sigma)^{12}} - \frac{4}{(r/\sigma)^6} \right\}, \quad . \quad . \quad . \quad . \quad . \quad (41)$$

where r is the distance between molecules and whence σ is the distance at which $\phi(r) = 0$. The temperature in the molecular units therefore is given by $T^* = kT/\epsilon$, the molar volume by $V^* = V/N\sigma^3$ and the pressure by $p^* = p\sigma^3/\epsilon$. To account for the quantum character of the gas, de Boer introduced a molecular quantum parameter, Λ^* , given by

$$\Lambda^* = h/\sigma\sqrt{m\epsilon}, \quad . \quad . \quad . \quad . \quad . \quad (42)$$

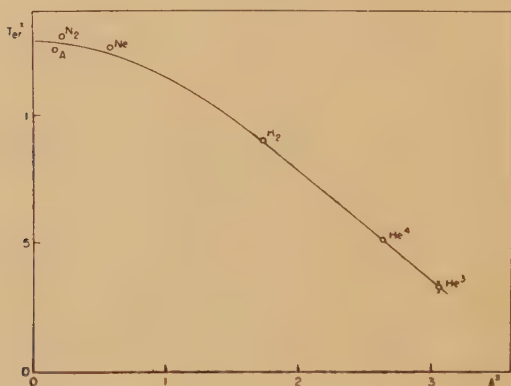
where Λ^* represents the ratio of the de Broglie wavelength of relative motion of two molecules with energy ϵ to the characteristic length σ . The equation of state therefore could be expressed as some function of the classical molecular parameters, p^* , V^* , and T^* , quoted above, and of the quantum parameter Λ^* . In order to calculate the properties of condensed ^3He , de Boer and Lunbeck adopted the semi-empirical process of plotting the

* A brief account of an alternative theory for the velocity of second sound in $^3\text{He} + ^4\text{He}$ solutions has been given by Koide and Usui (1951) at the Oxford Conference on Low Temperature Physics, August 1951. Pending fuller publication of the theory, however, comment is withheld.

values of the quantity of interest for gases whose properties were known and which follow the eqn. (41) as a function of the quantum parameter Λ^* and then extrapolating the curve to the appropriate value of Λ^* (3.05) for ^3He . The results shown in fig. 26 serve to illustrate this process, in which the critical temperature (expressed in molecular units, T_{cr}^*) is plotted as a function of Λ^* for A, Ne, N_2 , H_2 and ^4He . By extrapolating this curve to $\Lambda^*=3.05$, the authors could predict the critical temperature of ^3He . In this way de Boer and Lunbeck predicted that for ^3He the critical temperature, T_{cr} , would lie between the limits 3.1°K to 3.5°K and the critical pressure between 0.93 and 1.35 atm. The observed values, which were measured many months *after* de Boer and Lunbeck's papers were sent to press, were, as is described in § 4 (a) above, $T_{cr}=3.34^\circ\text{K}$ and $p_{cr}=1.15$ atm. In this way also de Boer and Lunbeck gave estimates for the molar volume at the absolute zero and for the vapour pressure equation. The latter they wrote as :

$$\log_{10} p_{cm} = -\frac{U_0}{RT} + 2.5 \log_{10} T + 1.01, \quad . \quad . \quad . \quad (43)$$

Fig. 26



Plot of the critical temperature, T_{cr}^* , in molecular units for various fluids as a function of the quantum parameter, Λ^* . Plot given by de Boer (Proc. Internat. Conf. on Phys. of very Low Temps., M.I.T., Sept. 1949, p. 38).

which is the usual thermodynamic expression without the term describing the effect of the thermal motion, a term which in ^4He also is small. The first term in this expression was calculated to be $-1.12/T$ by the method involving the quantum parameter, Λ^* , as indicated above, and the last term, the chemical constant, was calculated in the usual way for a perfect gas having mass number 3 *without* spin. The above equation for the vapour pressure described within a few per cent the results obtained by experiment.

These remarkable results indicated the satisfactory nature of de Boer and Lunbeck's approach to the problem of taking account of the zero-points motion of a system in which, as in the lighter gases, the zero-points

energy is more than a first order correction. It is of interest to note, moreover, that the semi-empirical method used was independent of any assumption with regard to the nature of the statistics of the assembly.

(b) *The Viscosity of Pure Liquid ^3He*

A theoretical study of the viscosity of pure ^3He has been carried out by Buckingham and Temperley (1950). These authors sought to explain the reported observed increase of the viscosity with decreasing temperature (Weinstock *et al.* 1949) by two alternative mechanisms. In the first they assumed that the liquid ^3He could be represented by a gas (rigid sphere and special interaction potential models were considered) and that as the temperature was reduced the collision cross section diminished due to the Ramsauer effect, thus increasing the mean free path and the viscosity. Taking account of the nuclear spin orientation, as has also been done by Halpern (1951) in viscosity studies, Buckingham and Temperley found that only the rigid sphere model in which the spins of each colliding pair of atoms are parallel gave the observed trend of viscosity with temperature (see also de Boer 1951 for further considerations of this). However the variation in the viscosity calculated in this way was small and in addition, as mentioned below in § 6 (c), no ferromagnetic effects such as would be associated with such spin parallelism have been observed, and consequently the authors rejected the Ramsauer effect as being the primary cause for the observed effects. Their second mechanism was one that follows from consideration of the viscosity of a degenerate Fermi-Dirac gas. For such a gas the effective collision cross section diminishes with diminishing temperature, due to the fact that the scattered states become increasingly occupied, as has been calculated in detail by Tomonaga (1938), and as a result the mean free path and hence the viscosity increase with diminishing temperature. The authors assumed therefore that liquid ^3He could be represented by a degenerate F-D gas, and its viscosity given by :

$$\eta = (1/15\pi^3)(2m\epsilon_0^5)^{1/2} \cdot \frac{1}{Q} \cdot \frac{1}{(kT)^2}, \quad \dots \dots (44)$$

where ϵ_0 is the Fermi energy and Q the scattering cross section. It is to be noted that this is fundamentally the same viewpoint as that taken earlier by Singwi and Kothari (1949) in their considerations of the viscosity of $^3\text{He} + ^4\text{He}$ solutions. By taking Q as given by the gas kinetic radius, and $\epsilon_0/k = 5^\circ \text{K}$, Buckingham and Temperley found that eqn. (44) above not only gave the observed trend of the viscosity with temperature, but also gave numerical values of the same order of magnitude as those reported by Weinstock *et al.* It would appear therefore that a quasi-gaseous model for liquid ^3He , as well as for liquid ^4He , gives a satisfactory picture of the liquid in the pure state as well as in solution at least so far as such properties as the viscosity, the distribution coefficient, the T_λ^s line in solutions, the partial vapour pressures in solutions and second sound are concerned, and that this quasi-gaseous model for ^3He must be one obeying the Fermi-Dirac statistics.

By considering the elementary excitations in liquid ^3He also to obey the Fermi-Dirac statistics, Pomeranchuk (1950) derived conclusions about various properties of the liquid (see §§ 6(d) and 6(e) below), and in particular arrived at the same variation for the viscosity with temperature as that given above in eqn. (44).

(c) *Ferromagnetism*

Since the ^3He nucleus possesses spin ($I=\frac{1}{2}$) with magnetic moment 2.12815 nuclear magnetons (see Anderson 1949), consideration of the exchange energy in ^3He assemblies is of importance. This has been discussed by Goldstein and Goldstein (1949) and by Pomeranchuk (1950). The former authors reported without giving any significant detail that, although the exchange energy alone favours the parallel arrangement of nuclear spins, in an assembly with a certain assumed potential field between atoms, no nuclear ferromagnetism would be expected. For a degenerate Fermi-Dirac gas, with which it seems appropriate to compare pure liquid ^3He , it follows that an antiparallel arrangement of spins must occur, as has been stressed by Pomeranchuk. An experimental search has been made, however, for possible ferromagnetism in liquid ^3He by Sydoriak and Hammel (1949), using an apparatus which could detect permeabilities of about $\mu \approx 2$. No ferromagnetic effects were observed in the temperature range 0.9° K to 2.5° K.

(d) *Entropy of Liquid ^3He*

Although no specific heat measurements have been made on pure liquid ^3He , many suggestions have been put forward regarding the temperature variation of the entropy of the liquid. Abraham *et al.* (1950) have made calculations of the entropy in the following way. First they calculated the entropy of the vapour from the Sackur-Tetrode equation :

$$S_{\text{vap}} = 2.5R \ln T - R \ln p_{\text{atmos}} + 1.5R \ln M - 2.314, \quad . \quad . \quad (45)$$

at certain chosen temperatures. In the above equation the contribution due to the nuclear spins, $R \ln 2$, is not included. From these vapour entropy values they subtracted the entropy of vaporization, which they had previously calculated (see § 4 (a) above), and hence obtained estimates for the entropy of the liquid at 1.0° K, 1.5° K, 2.0° K and 2.5° K, all of which temperatures were within the range of the original vapour pressure measurement. Their results are shown in fig. 27.

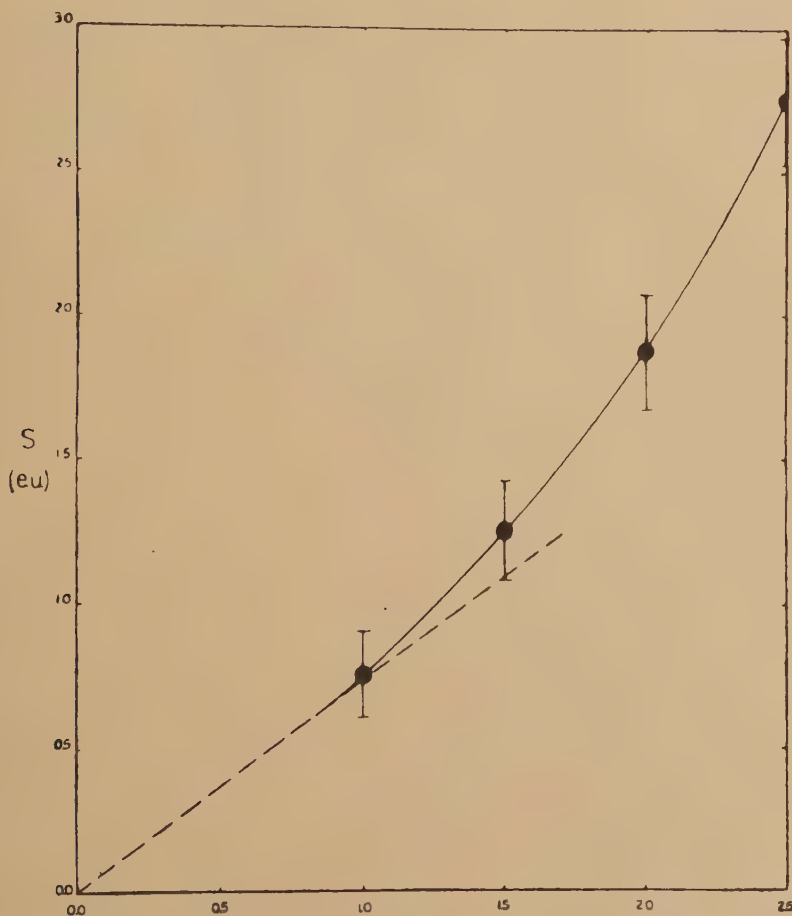
By considering the liquid ^3He at low temperatures ($T \leq 2^\circ \text{K}$) as a degenerate Fermi-Dirac assembly in which also phonon excitation is possible, the writer proposes that the results of the entropy evaluation given in fig. 27 can be interpreted as the sum of a linear term and of a cubic term in the temperature. The constants in such temperature function can be obtained from the results given in fig. 27 in the usual way (see e.g. Silvidi and Daunt 1950) by plotting S/T against T^2 . Such a plot should yield a straight line if the original assumption with regard to the temperature function is correct. For the data of fig. 27 such a

plot does yield a straight line, and from it the writer has deduced that the specific heat of liquid ^3He in the temperature range 1.0°K to 2.5°K could be represented by :

$$C = 0.68RT + 0.2RT^3 \text{ cal/mol/deg.} \quad (46)$$

The linear function has been inserted in fig. 27 by the broken line. Considerable caution must be taken in this interpretation due to the

Fig. 27



Plot of the entropy, S , of liquid ^3He against temperature, as calculated by Abraham *et al.* (1950) from vapour pressure measurements.

possible error in the original entropy evaluations, but it is of interest to note* that a perfect F-D gas with the ^3He liquid density would have

* Dr. R. B. Dingle has since kindly informed the writer of a paper by E. M. Lifshitz (*Jour. Exp. & Theor. Phys. U.S.S.R.*, **21**, 659, 1951) which suggests that an interpretation of vapour pressure data leads to the conclusion that the specific heat of liquid $^3\text{He} \approx 0.76RT$ cal/mol/deg. No other data on this paper are at present available to the writer.

$C \approx \pi^2 RT/2T_0 \approx RT$ cal/mol/deg, where T_0 , the F-D degeneracy temperature, is about 5°K . The absolute magnitude of the cubic term in eqn. (46) above is much larger than that experimentally obtained for liquid ^4He (Kramers 1951), but such a trend might be expected in view of the possibility of liquid ^3He having a greater compressibility than liquid ^4He .

In their considerations regarding the entropy of liquid ^3He Abraham *et al.* (1950) also made estimates of the entropy of the liquid at the absolute zero from the values they obtained for the chemical constant in their vapour pressure equation (eqn. (3)). Such a procedure is in effect making an extrapolation of the observed vapour pressure equation to the absolute zero. They found that such a procedure led to an evaluation of the entropy at the absolute zero of 0.42 entropy units. Such a result indicates that such an extrapolation of the vapour pressure curve is an invalid process. Abraham *et al.* concluded further that this result indicated the existence of a transition below 1.0°K , which is sufficient to account for this 0.42 units of entropy.

The existence of a possible transition in liquid ^3He , in a higher temperature range (1.0°K to 2.0°K), was suggested on general grounds by ter Haar (1949), who proposed amongst other possibilities that the λ -transition in liquid ^4He may be due to degeneracy effects in the Bose-Einstein statistics of the *modes of motion* rather than of the atoms and that in liquid ^3He the same process may be operative. ter Haar remarked further that such a transition, although evident in the specific heat, might not show superfluidity. The more recent data on the lack of superfluidity in liquid ^3He (see § 3 (a) above), do not rule out such a possibility, although it would appear from current information that the thermal excitations in ^3He are probably of the Fermi-Dirac type. Another possibility of a transition at about 2°K was put forward by Miller (1949) based on an interpretation of the first vapour pressure measurements of Sydoriak *et al.* (1949). The accuracy of the experimental data, however, probably was insufficient to allow too detailed an interpretation of the minor irregularities. It has been previously pointed out by the writer that an extrapolation of a plot of the triple points of Xe, Kr, D_2 , H_2 etc., expressed in molecular units, T_{tr}^* , (see de Boer's theory outlined above) against A^* passes exactly through the λ -temperature of ^4He , and would presumably indicate a possible transition in liquid ^3He at 1.0°K .

An experimental search has been made by Sydoriak and Hammel (1949) for possible transitions in liquid ^3He in the temperature range 0.84°K to 3.21°K by allowing a reservoir of the liquid to warm up slowly under approximately constant heat input and by watching for any irregularities in the observed vapour pressure as a function of the time of observation. If a λ -transition were to occur such a procedure would yield a point of inflexion in the p versus time curve. The authors reported no evidence for any irregularities, but no exact statement was made with regard to the sensitivity of the apparatus; nor is it clear that such a

procedure would give evidence for a transition for which the specific heat anomaly was more of a Schottky type rather than a λ -transition.

Direct measurement of the specific heat of liquid ^3He over as broad a temperature range as possible appears necessary to establish experimentally the actual processes operative in the liquid.

A further development of the theory of liquid ^3He has been made by Pomeranchuk (1950) who has supposed that the excited states in the liquid obey the Fermi-Dirac statistics. Since the Fermi-Dirac degeneracy temperature for a perfect gas of ^3He with the liquid density is about 5°K , only energies close to the Fermi surface need be considered which leads to an estimate for the number, n , of excitations per c.c. given by $n \approx NT/T_0$, where T_0 is the Fermi-Dirac degeneracy temperature and N the number of atoms per c.c. On such a model the internal energy, u , is given by :

$$u = u_0 + \frac{1}{2}aT^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad (47)$$

where $a = yp_0^2/\hbar^3v$ ($y \approx \pi^{-2}$ and p_0 = the radius of the Fermi sphere). This yields a heat capacity $C = aT$, a linear relationship which had already been explicitly proposed by Singwi and Kothari (1949) and which is the familiar result for degenerate Fermi-Dirac statistics. Pomeranchuk also gave the temperature variation of the viscosity and heat conductivity of such a Fermi-Dirac assembly, as given also by Singwi and Kothari (1949) and by Buckingham and Temperley (1950) (see §§ 5(a) and 6(b) above).

(e) Solid ^3He

In liquid ^3He the apparent linear variation of the entropy with temperature at low temperature (see section above), taken together with many other properties of the pure liquid and of the solutions of ^3He in liquid ^4He , strongly suggests that the liquid can be regarded in the pure form as a degenerate Fermi-Dirac system of a quasi-gaseous character, as has been pointed out by many authors. Such a degenerate system would have anti-parallel spin arrangement.

In the solid state, however, the effect of the exchange energy on the spin arrangement would be different from that in the liquid phase and Pomeranchuk (1950) has suggested that the exchange effects in the solid at any available temperature are negligibly small owing to the fact that the amplitude of vibration must be less than the interatomic distance, b . He proposed therefore that in the solid the nuclear spins can be regarded as essentially 'free', giving a contribution to the entropy of $R \ln 2$ entropy units. This free orientation of spin, he proposed, would be valid until temperatures are reached where nuclear dipole-dipole interactions are of importance, i.e. down to a characteristic temperature, T_n , given by :

$$T_n \approx \mu^2/kb^3 \approx 10^{-7}^\circ \text{K},$$

where μ is the nuclear magnetic moment. Superposed on this $R \ln 2$ term for the entropy would be a term $\frac{12}{5}\pi^4 R(T/\theta)^2$, giving the lattice

entropy which Pomeranchuk suggested would be negligible below 1°K . The entropy curves for solid and liquid ^3He , therefore, would *cross* at the temperature (about 1°K) where S_{liq} reached a value of approximately $R \ln 2$. Below this temperature S_{sol} would be *greater* than S_{liq} and hence heat should be evolved at isothermal melting. Also since the specific volume of the liquid is larger than that of the solid, an inspection of the Clausius-Clapeyron equation for the melting line,

$$dp/dT = R(S_{\text{sol}} - S_{\text{liq}})/(V_{\text{sol}} - V_{\text{liq}}),$$

shows that for temperatures below 1°K , where Pomeranchuk suggests $S_{\text{sol}} > S_{\text{liq}}$, the term dp/dT must be negative, i.e. as the temperature is reduced below 1°K , the melting pressure *increases*. Whether the measurements of the melting curve reported by Abraham, Osborne and Weinstock (1951) below 0.5°K (see § 4 (b) above) can be interpreted as confirmation of this theory is as yet an open question. Further measurements would be of value. According to Pomeranchuk, this increase in the melting pressure with decreasing temperature would continue until temperatures about T_{H} were reached, below which temperature the correlations between the spins would make S_{sol} tend to zero and hence dp/dT tend to zero.

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